DOI: https://doi.org/10.57233/ijsgs.v12i2.1114 ISSNp: 2488-9229; ISSNe: 3027-1118

IJSGS FUGUSAU VOL . 12(2) WEBSITE: https://fugus-ijsgs.com.ng

INTERNATIONAL JOURNAL OF SCIENCE FOR GLOBAL SUSTAINABILITY
(A PUBLICATION OF FACULTY OF SCIENCE, FEDERAL UNIVERSITY GUSAU, NIGERIA)

Comparative Optimization of Methyl Red Dye Removal from Aqueous Solution Using KOH-Modified Orange Peel and Moringa Leaf Biomass

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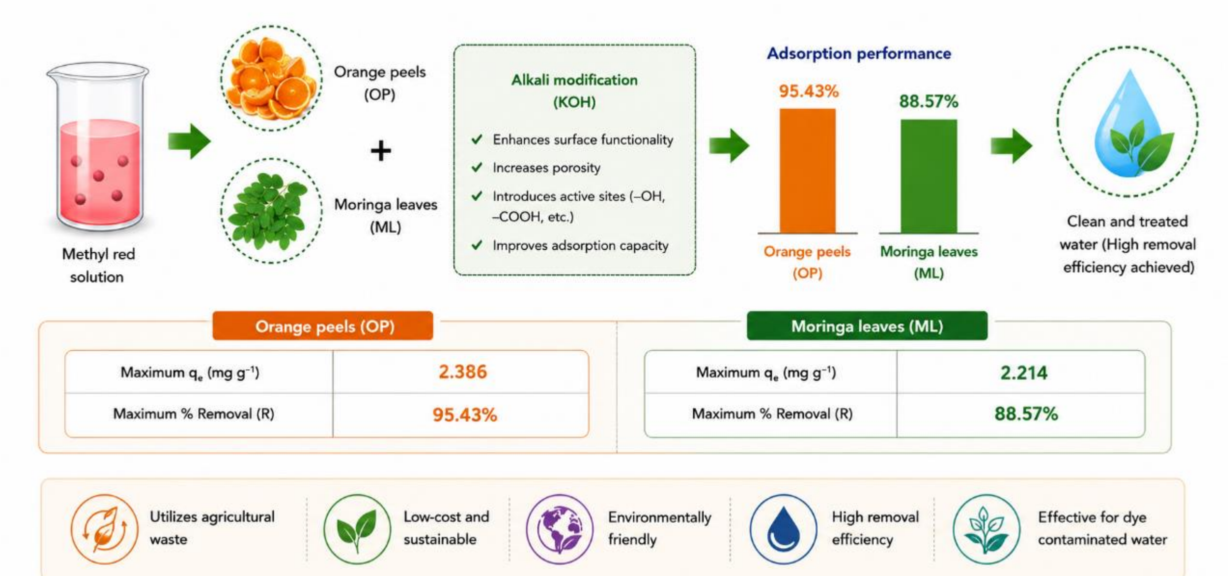
Received on: April 2026 **Revised and Accepted on:** June, 2026 **Published on:** July, 2026

ABSTRACT

The discharge of dye-containing wastewater from industrial activities poses significant environmental challenges due to the persistence, visibility, and potential toxicity of synthetic dyes. This study compared the adsorption of methyl red from aqueous media using potassium hydroxide (KOH)-modified orange peels and *Moringa oleifera* leaves as low-cost biosorbents. The effects of initial dye concentration (2–10 mg L^{-1}), adsorbent dosage (0.1–0.5 g), solution pH (3–9), contact time (10–1440 min), and temperature (40–50 °C) on adsorption performance were investigated. The point of zero charge (pH_{pzc}) was determined to be approximately 5.1 for orange peels and 6.6 for moringa leaves, indicating differences in surface charge characteristics. Adsorption performance was evaluated using adsorption capacity (q_e) and percentage removal (%R). Orange peels consistently exhibited superior adsorption performance across most operational conditions. Maximum adsorption capacities of 2.386 mg g^{-1} and 2.214 mg g^{-1} were obtained for orange peels and moringa leaves while maximum removal efficiencies reached 95.43% and 88.57%, respectively. Adsorption was favored under acidic conditions, increased with contact time up to equilibrium, and generally improved with increasing temperature. The enhanced performance of orange peels was attributed to their lignocellulosic composition, abundance of surface functional groups, and improved accessibility of adsorption sites following alkali modification. The findings demonstrate that both biosorbents are effective and sustainable materials for methyl red removal; however, KOH-modified orange peels showed greater adsorption capacity and operational stability. These results highlight the potential of agricultural wastes as affordable alternatives for dye-contaminated wastewater treatment.

Keywords: Methyl red, Biosorption, Agricultural waste adsorbents, KOH modification, Dye removal

Graphical Abstract



1.0 INTRODUCTION

Access to safe and adequate water is one of the biggest environmental and public health challenges worldwide. Rapid industrialization, urbanization, population growth, and poor wastewater treatment facilities have significantly increased the release of untreated or

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partially treated waste into rivers, lakes, and groundwater. According to the United Nations World Water Development Report 2024, billions of people suffer from declining water quality due to pollution, inadequate sanitation, and insufficient wastewater management, especially in developing countries (United Nations World Water Assessment Programme [UNWWAP], 2024). Industrial wastewater plays a major role in this issue because it often contains harmful substances like persistent organic pollutants, heavy metals, pharmaceuticals, and synthetic dyes that endanger aquatic ecosystems and human health. As a result, developing sustainable, efficient, and cost-effective wastewater treatment technologies is now a key research focus globally (Crini and Lichtfouse, 2019; Aragaw, 2021).

Among industrial contaminants, synthetic dyes are of particular concern because of their complex aromatic structures, high water solubility, resistance to biodegradation, and persistence in aquatic environments. Dye-containing wastewater is generated from numerous industrial sectors, including textile manufacturing, paper production, leather processing, cosmetics, food industries, and analytical laboratories. Even at low concentrations, dyes impart intense colour to receiving waters, reduce light penetration, inhibit photosynthetic activity, alter dissolved oxygen dynamics, and ultimately disrupt aquatic ecosystems. Many azo dyes may also undergo reductive transformation under environmental conditions, producing aromatic amines with potential ecological and toxicological implications. Owing to these characteristics, dye-contaminated wastewater has become a significant environmental issue requiring effective treatment before discharge (Aragaw, 2021; Andriambahiny *et al.,* 2025). Methyl red, a monoazo dye widely used as an acid–base indicator and analytical reagent, has frequently been employed as a model pollutant for evaluating the adsorption performance of low-cost biosorbents because its physicochemical properties are representative of many structurally related azo dyes encountered in industrial wastewater (Deshmukh *et al.,* 2022).

Several technologies exist for treating dye-laden wastewater, including coagulation, membrane filtration, electrochemical oxidation, photocatalysis, biological treatment, and advanced oxidation processes. While these methods can achieve high removal rates under certain conditions, many face challenges such as high capital and operating costs, membrane fouling, sludge creation, significant energy use, or incomplete breakdown of pollutants. These problems are especially acute in developing countries, where low-cost, energy-efficient, and decentralized treatment solutions are needed for effective wastewater management (Crini and Lichtfouse, 2019; Andriambahiny *et al.,* 2025). Among treatment methods, adsorption is particularly appealing because it is simple to operate, highly effective, easy to design, and capable of removing contaminants from a wide range of concentrations. The adsorption process involves pollutants gathering on the surface of a solid adsorbent through various interactions, including electrostatic attraction, hydrogen bonding, van der Waals forces, and pore filling. As a result, adsorption has become a widely researched technique for dye removal from water, especially when using inexpensive and eco-friendly adsorbents (Aragaw, 2021; Yadav *et al.,* 2024).

Commercial activated carbon remains one of the most effective adsorbents for dye removal because of its exceptionally high surface area and well-developed pore structure. However, its widespread application is often restricted by high production, regeneration, and disposal costs. In recent years, increasing attention has therefore been directed towards the development of low-cost biosorbents derived from agricultural residues and other lignocellulosic wastes. These materials are renewable, biodegradable, abundant, and consistent with circular economy principles that promote the conversion of agricultural waste into value-added environmental remediation materials. Chemical modification of these biomasses using activating agents such as potassium hydroxide (KOH) has been shown to improve adsorption performance by increasing pore accessibility, removing surface impurities, and exposing oxygen containing functional groups that participate in pollutant uptake. Consequently, chemically modified agricultural wastes have emerged as promising alternatives to commercial activated carbon for sustainable wastewater treatment applications (Benettayeb *et al.*, 2022; Andriambahiny *et al.,* 2025; Yadav *et al.,* 2024).

Orange peels represent one of the most abundant agro-industrial wastes generated globally from fruit processing and household consumption. Their structure, mainly made of cellulose, hemicellulose, lignin, and pectin, offers many hydroxyl and carboxyl functional groups that can interact with dye molecules through various adsorption methods. Recent research shows that chemical modifications to orange peel biomass can greatly boost adsorption efficiency by enhancing pore development, surface roughness, and the availability of active sites for adsorption. Similarly, Moringa oleifera leaves have gained attention as sustainable biosorbents due to their rich content of proteins, polysaccharides, polyphenols, and functional groups that help remove pollutants. In addition to their adsorption abilities,

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materials derived from moringa are inexpensive, biodegradable, readily available in tropical areas, and compatible with sustainable water treatment approaches. Thus, both orange peels and Moringa oleifera leaves are emerging as promising sources for developing eco-friendly adsorbents for wastewater treatment (Benettayeb *et al.,* 2022; Yadav *et al.,* 2024).

Although many studies have investigated dye adsorption using agricultural and plant-based biosorbents, direct comparisons between chemically modified orange peels and moringa leaves under the same experimental conditions are limited. Additionally, there are relatively few studies that systematically assess how initial dye concentration, adsorbent dosage, solution pH, contact time, and temperature collectively affect methyl red removal using these two widely available biomass resources. Therefore, this study aims to compare the removal of methyl red from water using KOH-modified orange peels and moringa leaves as low-cost biosorbents. By examining key operational parameters under the same conditions, the research identifies the more effective biosorbent and provides locally relevant information for affordable and sustainable wastewater treatment strategies.

2.0 METHODOLOGY

2.1 Materials and Chemicals

Methyl red dye (analytical grade) was used as the model adsorbate without further purification. Potassium hydroxide (KOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), and distilled water were used throughout the study. Orange peels and fresh *Moringa oleifera* leaves were selected as precursor biomass materials for adsorbent preparation. The principal equipment used included a UV–Visible spectrophotometer for dye concentration analysis, a digital pH meter for solution pH adjustment and monitoring, a magnetic stirrer for agitation, an analytical balance for accurate weighing, a drying oven for biomass dehydration, and standard laboratory glassware such as beakers, measuring cylinders, conical flasks, funnels, and filtration apparatus.

2.2 Preparation of Raw Adsorbents

Orange peels were collected from fruit vendors within Ibadan, Nigeria, while fresh *Moringa oleifera* leaves were obtained locally. The collected biomass materials were thoroughly washed with tap water followed by distilled water to remove adhering dirt, soluble impurities, and surface contaminants. The washed orange peels were oven-dried at 60 °C for 32 hrs, while moringa leaves were dried at the same temperature for 20 hrs. After drying, both materials were separately crushed, ground, and sieved to obtain smaller uniform particles suitable for adsorption studies. The prepared raw biomasses were stored in airtight containers prior to chemical modification.

2.3 Preparation of KOH Solution

A dilute potassium hydroxide activating solution was prepared by dissolving 5.4 g of KOH pellets in distilled water and making the final volume up to 1 L in a volumetric flask. The solution was mixed thoroughly until complete dissolution was achieved.

2.4 Chemical Modification of Adsorbents

To enhance adsorption performance, the prepared raw biomasses were chemically activated using KOH solution. Fifty grams (50 g) each of dried orange peel powder and dried moringa leaf powder were separately transferred into clean beakers containing 300 mL of the KOH solution. Each suspension was stirred continuously for 2 hrs using a magnetic stirrer to ensure effective contact between the activating agent and biomass surface. Thereafter, the mixtures were filtered, and the recovered solid residues were oven-dried at 60 °C. Orange peel residue was dried for 30 hrs, while moringa leaf residue was dried for 24 hrs. The dried modified materials were further pulverized and sieved through a 425 µm mesh sieve to obtain uniform particle sizes. The final KOH-modified adsorbents were stored in airtight containers and labelled as modified orange peel (MOP) and modified moringa leaf (MML), respectively.

2.5 Batch Adsorption Experiments

Batch adsorption experiments were conducted to evaluate the removal of methyl red dye from aqueous solution using the prepared adsorbents. Unless otherwise stated, 0.1 g of adsorbent was contacted with 25 mL dye solution in stoppered bottles under controlled conditions.

After adsorption, suspensions were filtered using Whatman No. 1 filter paper, and the residual methyl red concentration in the filtrate was determined using a UV–Visible spectrophotometer at 435 nm.

The adsorption capacity (q_e, mg g^{-1}) and percentage removal (%R) of methyl red were calculated using Equations (1) and (2), respectively.

$$q_e = \frac{[(C_o - C_e)V]}{W} \quad (1)$$

$$\%R = \left[\frac{C_o - C_e}{C_o}\right] \times 100 \quad (2)$$

where q_e is the adsorption capacity (mg g^{-1}), C_o is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration (mg L^{-1}), V is the volume of the dye solution (L), and W is the mass of adsorbent used (g). Percentage removal (%R) represents the fraction of

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methyl red removed from solution at equilibrium relative to its initial concentration.

2.6 Effect of Initial Dye Concentration

The influence of initial methyl red concentration on adsorption performance was investigated by varying the dye concentration while maintaining constant adsorbent dosage, pH, temperature, and contact time.

2.7 Effect of Adsorbent Dosage

To determine the effect of adsorbent dosage, varying masses of adsorbent were introduced into a fixed volume and concentration of methyl red solution under constant experimental conditions.

2.8 Effect of Solution pH

The effect of pH on methyl red adsorption was examined over a pH range of 3–10. The pH of each dye solution was adjusted using 0.1 M HCl or 0.1 M NaOH prior to adsorption. For each run, 0.1 g adsorbent was mixed with 25 mL of 25 mg L^{-1} methyl red solution.

2.9 Effect of Contact Time

The influence of contact time was evaluated by agitating adsorbent–adsorbate mixtures for different time intervals of 10, 30, 60, 120, 240, 480, 720, 1080, and 1440 min under constant conditions.

2.10 Effect of Temperature

The effect of temperature on adsorption was studied at selected temperatures, including 40 °C and 50 °C, to evaluate the thermal dependence of the adsorption process.

2.11 Data Treatment and Performance Evaluation

Experimental adsorption data were evaluated using adsorption capacity (q_e, mg g^{-1}) and percentage dye removal (%R) as primary performance indicators. Residual methyl red concentrations obtained from UV–Visible spectrophotometric measurements were used to determine the extent of dye uptake by the prepared adsorbents under different operating conditions. Comparative assessment of KOH-modified orange peels and KOH-modified moringa leaves was based on observed changes in adsorption performance as a function of initial dye concentration, adsorbent dosage, solution pH, contact time, and temperature rather than inferential statistical significance testing. Optimum operating conditions for each adsorbent were identified from the highest observed adsorption capacity and/or dye removal efficiency.

3.0 RESULTS AND DISCUSSION

3.1 Point of Zero Charge (pH_{pzc})

The point of zero charge (pH_{pzc}) is the pH at which the net surface charge of an adsorbent becomes neutral. At solution pH values below the pH_{pzc}, the adsorbent surface is predominantly protonated and positively charged, whereas at pH values above the pH_{pzc}, deprotonation occurs and the surface becomes negatively charged. This parameter is important because it governs electrostatic attraction or repulsion between the adsorbent surface and ionic dye species (Teweldebrihan and Dinka, 2024) The pH_{pzc} values obtained in this study were 5.1 for KOH-modified orange peels and 6.6 for KOH-modified moringa leaves (Table 1). The trend of pH_{pzc} of the prepared adsorbents is displayed in Figure 1. The lower pH_{pzc} of orange peels indicates a relatively more acidic surface, which may be attributed to the presence of carboxylic, hydroxyl, and phenolic groups commonly associated with citrus biomass. Similar pH_{pzc} values have been reported for lignocellulosic citrus wastes used as adsorbents, where acidic surface groups enhanced anionic dye interactions under mildly acidic conditions (Teweldebrihan and Dinka, 2024).

Table 1: Point of Zero Charge of the Prepared Adsorbents

Adsorbent	pH_{pzc}
KOH-modified orange peels	5.1
KOH-modified moringa leaves	6.6

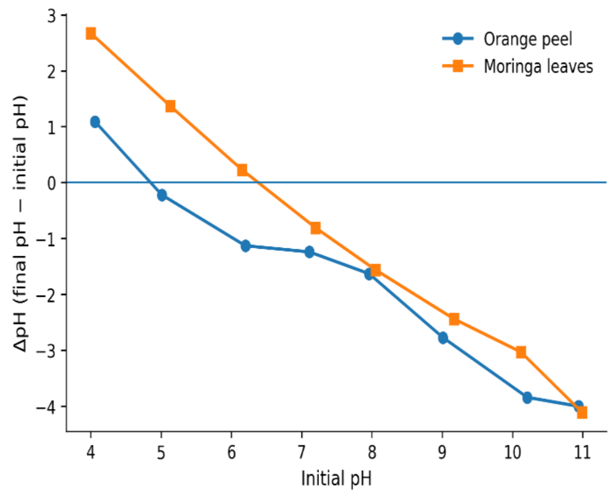

Figure 1: Determination of the point of zero charge (pH_{pzc}) of alkali-modified orange peels and moringa leaves.

The pH_{pzc} of moringa leaves (6.6) suggests a comparatively less acidic surface. This may arise from the presence of proteins and other nitrogen-containing biomolecules that contribute to a higher surface basicity. The higher pH_{pzc} value of moringa leaves relative to orange peels suggests differences in surface functional groups and charge characteristics, which may influence dye to surface interactions under varying pH conditions. Similar variations in pH_{pzc} among agricultural biosorbents have been reported in previous adsorption studies (Teweldebrihan and Dinka, 2024). For methyl red adsorption, these values imply that orange peels would be positively charged below pH 5.1 and therefore more favourable for adsorption of anionic dye species through electrostatic attraction. Likewise, moringa leaves would be positively charged below pH 6.6. However, the lower pH_{pzc} of orange peels may favour adsorption near mildly acidic pH where both protonation and accessibility of functional groups are optimized. Overall, the pH_{pzc} data provide a useful basis for interpreting the pH-dependent adsorption behaviour observed later in this study.

3.2 Effect of Initial Dye Concentration

The effect of initial methyl red concentration on adsorption performance is presented in Table 2 while Figure 2 shows the trend. For orange peels, adsorption capacity increased steadily from 0.436 mg g^{-1} (87.14%) at 2 mg L^{-1} to 1.536 mg g^{-1} (61.43%) at 10 mg L^{-1}. Moringa leaves exhibited a different trend, with adsorption capacity increasing from 0.129 mg g^{-1} (25.71%) to a maximum of 1.721 mg g^{-1} (86.07%) at 8 mg L^{-1} before declining to 0.964 mg g^{-1} (38.57%) at 10 mg L^{-1}.

Table 2. Effect of initial methyl red concentration on adsorption performance

Initial Concentration (mg L^{-1})	Orange Peels q_e (%R)	Moringa Leaves q_e (%R)
2	0.436 (87.14)	0.129 (25.71)
4	0.864 (86.43)	0.443 (44.29)
6	1.157 (77.14)	0.864 (57.62)
8	1.293 (64.64)	1.721 (86.07)
10	1.536 (61.43)	0.964 (38.57)

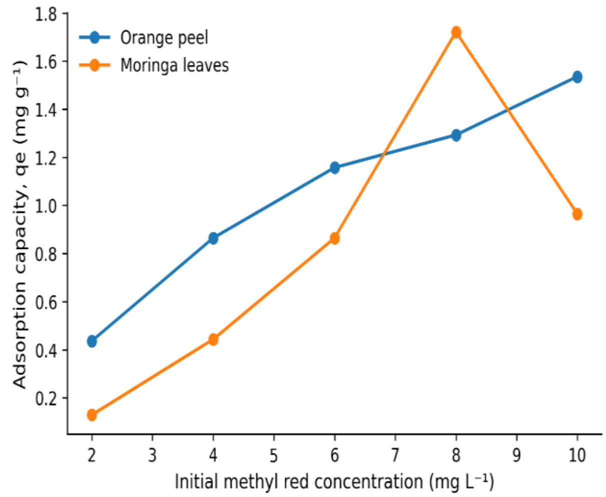

Figure 2: Effect of initial methyl red concentration on the adsorption capacity of alkali-modified orange peels and moringa leaves.

The observed increase in adsorption capacity with increasing dye concentration can be attributed to the higher concentration gradient between the bulk solution and the adsorbent surface, which enhances mass transfer and increases the probability of dye molecules interacting with available adsorption sites. Similar behaviour has been reported for methyl red adsorption onto biomass-derived adsorbents, where increasing initial dye concentration provides a greater driving force for mass transfer until progressive saturation of available adsorption sites occurs (Amari *et al.*, 2023). Although adsorption capacity increased for orange peels across the concentration range, the percentage removal decreased from 87.14% to 61.43%. This indicates that while more dye was adsorbed at higher concentrations, the number of available adsorption sites became progressively insufficient relative to the increasing dye load. Consequently, a smaller fraction of the total dye present in solution was removed. Comparable observations have been reported for low-cost biosorbents employed in methyl red removal from aqueous solutions (Teweldebrihan and Dinka, 2024). Moringa leaves exhibited maximum adsorption at 8 mg L^{-1}, after which both adsorption capacity and removal efficiency declined. This behaviour suggests earlier saturation of active sites and possible competition among dye molecules for limited adsorption sites at high concentrations. From a practical perspective, orange peels showed higher operational stability across the investigated concentration range, making them more suitable for treatment systems where influent dye concentrations may fluctuate.

3.3 Effect of Adsorbent Dosage

The influence of adsorbent dosage on methyl red adsorption is presented in Table 3 while the trend is displayed in Figure 3. For orange peels, adsorption capacity decreased from 1.129 mg g^{-1} (45.14%) at 0.1 g dosage to 0.014 mg g^{-1} (2.86%) at 0.5 g. A similar trend was observed for moringa leaves, where adsorption capacity declined from 0.857 mg g^{-1} (34.29%) at 0.1 g to 0.029 mg g^{-1} (5.71%) at 0.5 g.

Table 3. Effect of adsorbent dosage on adsorption performance

Dosage (g)	Orange Peels q_e (%R)	Moringa Leaves q_e (%R)
0.1	1.129 (45.14)	0.857 (34.29)
0.2	0.514 (41.14)	0.336 (26.86)
0.3	0.224 (26.86)	0.136 (16.29)
0.4	0.052 (8.29)	0.152 (24.29)
0.5	0.014 (2.86)	0.029 (5.71)

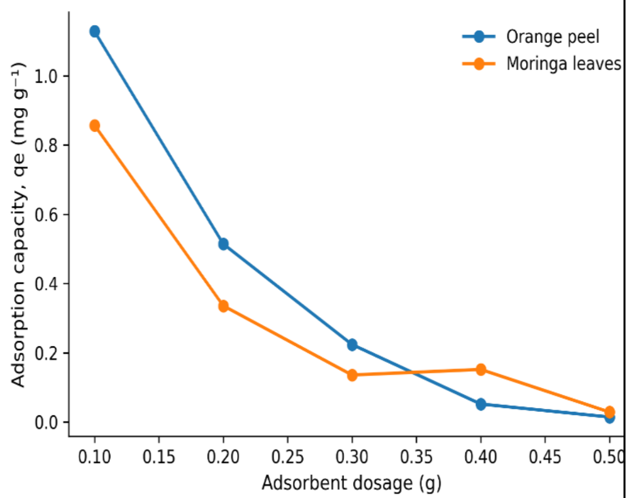

Figure 3: Effect of adsorbent dosage on the adsorption capacity of alkali-modified orange peels and moringa leaves.

The decline in adsorption capacity with increasing adsorbent dosage is a common feature of adsorption systems operated at constant dye concentration. Under such conditions, increasing the mass of adsorbent increases the number of available adsorption sites, but the amount of dye present becomes insufficient to occupy all sites effectively. As a result, the amount of dye adsorbed per unit mass decreases. Similar trends have been reported for methyl red adsorption using biomass-derived adsorbents, where increasing adsorbent dosage improved overall dye removal but decreased the equilibrium adsorption capacity (q_e) because of the underutilization of available adsorption sites (Khalfaoui *et al.,* 2022). Another factor contributing to reduced adsorption capacity at higher dosage is particle aggregation. Increased adsorbent loading may promote overlapping of adsorption sites and reduce the effective surface area available for interaction with dye molecules. Consequently, a lower proportion of active sites participates in adsorption.

For both adsorbents, the highest adsorption capacity was achieved at 0.1 g, indicating that lower adsorbent dosage provided the most efficient utilization of available adsorption sites under the experimental conditions employed. Orange peels maintained higher adsorption capacities than moringa leaves across most dosage levels, further demonstrating their stronger affinity toward methyl red.

3.4 Effect of Contact Time

The effect of contact time on methyl red adsorption by KOH-modified orange peels and moringa leaves is presented in Table 4, while the trend is displayed in Figure 4. For orange peels, adsorption capacity increased from 0.429 mg g^{-1} (17.14%) at 10 min to a maximum of 1.536 mg g^{-1} (61.43%) at 240 min, after which a gradual decline was observed with prolonged contact time. Similarly, adsorption by moringa leaves increased from 0.071 mg g^{-1} (2.86%) at 10 min to 0.964 mg g^{-1} (38.57%) at 240 min before declining slightly at longer contact periods.

Table 4. Effect of contact time on adsorption performance

Time (min)	Orange Peels q_e (%R)	Moringa Leaves q_e (%R)
10	0.429 (17.14)	0.071 (2.86)
30	0.571 (22.86)	0.221 (8.86)
60	0.929 (37.14)	0.357 (14.29)
120	1.414 (56.57)	0.714 (28.57)
240	1.536 (61.43)	0.964 (38.57)
480	1.436 (57.43)	0.929 (37.14)
720	1.414 (56.57)	0.857 (34.29)
1080	1.357 (54.29)	0.886 (35.43)
1440	1.107 (44.29)	0.686 (27.43)

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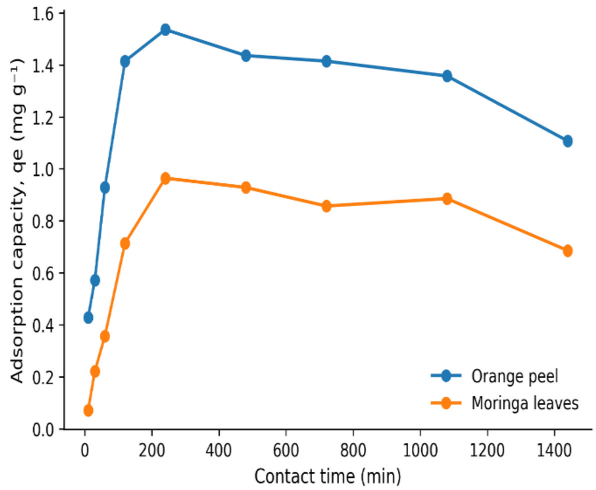

Figure 4: Effect of contact time on the adsorption capacity of alkali-modified orange peels and moringa leaves.

The rapid increase in adsorption capacity during the first 240 min indicates the availability of a large number of vacant adsorption sites and a strong concentration gradient between the solution and adsorbent surface. Under these conditions, methyl red molecules were readily transferred from solution to accessible active sites, resulting in rapid adsorption. Similar behaviour has been widely reported for dye adsorption onto biomass-derived adsorbents, where adsorption proceeds rapidly during the initial stages before gradually approaching equilibrium (Ho and McKay, 1999)**.** Beyond 240 min, both adsorption capacity and removal efficiency decreased slightly. This behaviour suggests that equilibrium had been attained and that prolonged contact may indicate partial desorption or redistribution of weakly bound dye molecules on the heterogeneous adsorbent surface. Similar reductions after equilibrium have been observed in methyl red adsorption systems**,** where adsorption–desorption processes occur simultaneously after saturation of the most accessible adsorption sites (Deshmukh *et al.*, 2022).

Throughout the experimental period, orange peels exhibited higher adsorption capacities and removal efficiencies than moringa leaves. At the optimum contact time of 240 min, orange peels achieved 1.536 mg g^{-1} and 61.43% removal compared with 0.964 mg g^{-1} and 38.57% removal for moringa leaves. This finding suggests that orange peels possessed a greater number of accessible active sites and stronger affinity for methyl red adsorption under the conditions investigated. Therefore, 240 min was identified as the optimum contact time for both adsorbents.

3.5 Effect of Solution pH

The effect of solution pH on methyl red adsorption is presented in Table 5, while the trend of this effect can be seen in Figure 5. Adsorption performance was strongly influenced by pH for both adsorbents. For orange peels, adsorption capacity increased from 2.143 mg g^{-1} (85.71%) at pH 3 to a maximum of 2.386 mg g^{-1} (95.43%) at pH 5, followed by a gradual decline to 1.307 mg g^{-1} (52.29%) at pH 9. In contrast, moringa leaves exhibited maximum adsorption at pH 3, with adsorption capacity decreasing continuously from 2.214 mg g^{-1} (88.57%) to 0.714 mg g^{-1} (28.57%) as pH increased to 9.

Table 5. Effect of solution pH on adsorption performance

pH	Orange Peels q_e (%R)	Moringa Leaves q_e (%R)
3	2.143 (85.71)	2.214 (88.57)
4	2.314 (92.57)	2.014 (80.57)
5	2.386 (95.43)	1.736 (69.43)
6	1.986 (79.43)	1.464 (58.57)
7	1.807 (72.29)	1.214 (48.57)
8	1.536 (61.43)	0.964 (38.57)
9	1.307 (52.29)	0.714 (28.57)

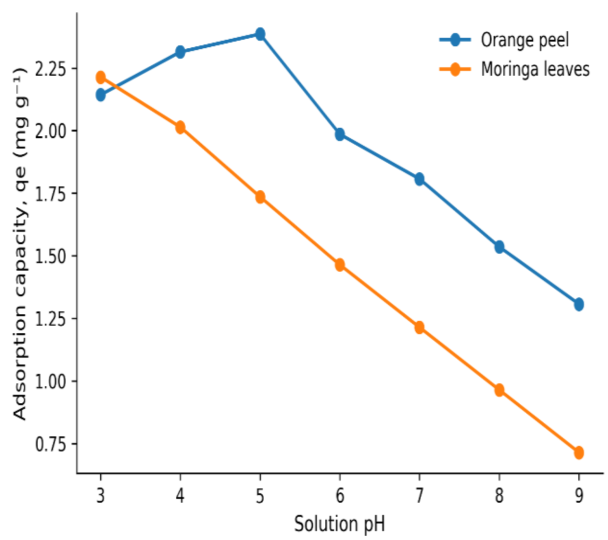

Figure 5: Effect of solution pH on the adsorption capacity of alkali-modified orange peels and moringa leaves.

The strong influence of pH on adsorption behaviour confirms the important role of surface charge and adsorbate ionization in controlling methyl red uptake. The maximum adsorption capacity observed for orange peels at pH 5 is particularly significant because this value closely corresponds to the pH_{pzc} of the adsorbent (5.1). At this pH, the adsorbent surface remains sufficiently protonated to promote favourable electrostatic

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interactions while minimizing excessive competition from hydrogen ions. Consequently, adsorption capacity and removal efficiency reached their highest values under mildly acidic conditions.

For moringa leaves, adsorption was highest at pH 3 and declined progressively as pH increased. This behaviour indicates a stronger dependence on protonated surface sites and suggests that adsorption becomes less favourable as surface deprotonation increases. The reduction in adsorption capacity observed at alkaline pH for both adsorbents may be attributed to increased electrostatic repulsion and competition between hydroxyl ions and dye molecules for available adsorption sites. Similar pH-dependent behaviour has been reported for the adsorption of methyl red onto biomass-derived adsorbents, where adsorption decreased with increasing solution pH because of reduced electrostatic attraction and competition from hydroxyl ions (Khalfaoui *et al.*, 2022).

The results also agree with the pH_{pzc} values determined for the adsorbents. Orange peels (pH_{pzc} of 5.1) retained relatively high adsorption capacity over a broader pH range than moringa leaves (pH_{pzc} of 6.6), indicating greater tolerance to pH variation. From an operational perspective, acidic conditions were most favourable for methyl red removal, with optimum adsorption occurring at pH 5 for orange peels and pH 3 for moringa leaves. However, orange peels maintained superior adsorption performance across the entire pH range investigated, highlighting their greater practical applicability for wastewater treatment systems where pH conditions may fluctuate.

3.6 Effect of Temperature

Temperature is an important operational parameter in adsorption processes because it influences the mobility of adsorbate molecules, diffusion rates, solution viscosity, and the interaction between adsorbate and adsorbent surfaces. The effect of temperature on methyl red adsorption by KOH-modified orange peels and moringa leaves was investigated at 40 °C and 50 °C, and the results are presented in Table 6 and Figure 6a and b.

Table 6. Effect of temperature on methyl red adsorption by alkali-modified orange peels and moringa leaves

Co ($mg\ L^{-1}$)	Orange Peel 40 °C q_e (%R)	Orange Peel 50 °C q_e (%R)	Moringa Leaves 40 °C q_e (%R)	Moringa Leaves 50 °C q_e (%R)
2	0.421 (84.29)	0.429 (85.71)	0.193 (38.57)	0.229 (45.71)
4	0.886 (88.57)	0.907 (90.71)	0.150 (15.00)	0.286 (28.57)
6	1.221 (81.43)	1.321 (88.10)	0.243 (16.19)	0.293 (19.52)
8	1.457 (72.86)	1.564 (78.21)	1.821 (91.07)	1.864 (93.21)
10	1.829 (73.14)	1.936 (77.43)	1.143 (45.71)	1.829 (73.14)

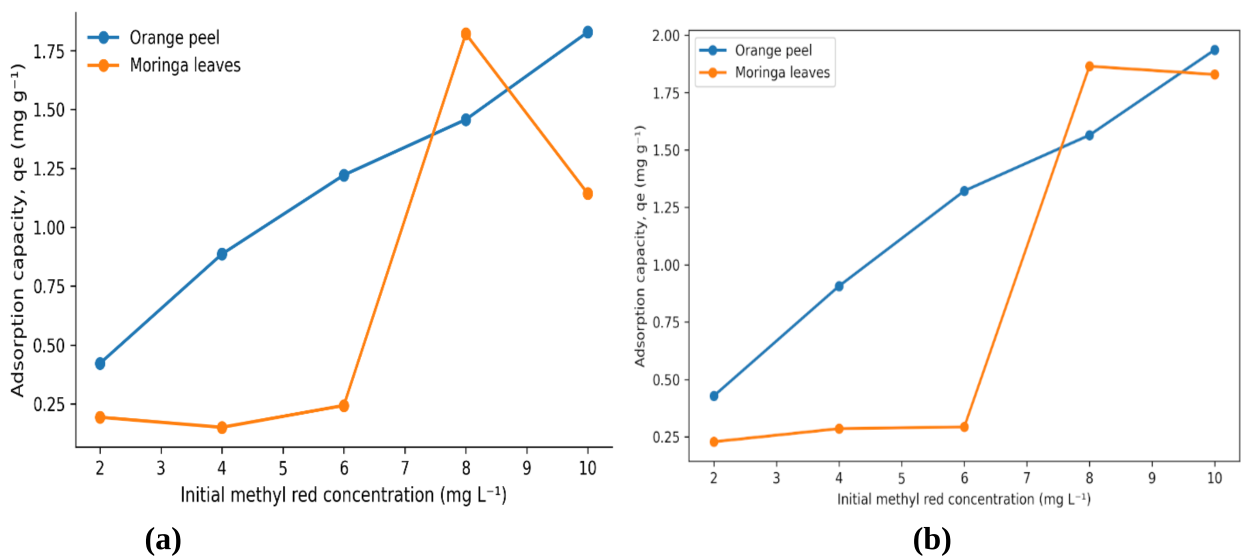

Figure 6: Effect of temperature on the adsorption capacity of alkali-modified orange peels and moringa leaves: (a) 40 °C and (b) 50 °C.

For orange peels, adsorption capacity increased consistently with increasing temperature-- across the concentration range investigated. At 10 mg L⁻¹, adsorption capacity increased from 1.829 mg g^{-1} (73.14%) at 40 °C to 1.936 mg g^{-1} (77.43%) at 50 °C. Similarly, moringa leaves showed improved adsorption performance at elevated temperature, particularly at higher concentrations where adsorption capacity increased from 1.143 mg g^{-1} (45.71%) to 1.829 mg g^{-1} (73.14%) at 10 mg L^{-1}. The enhancement in adsorption performance with increasing temperature suggests that higher thermal energy promoted the transport of methyl red molecules from solution to the adsorbent surface. Increase in temperature reduces the viscosity of solutions and enhances mobility of molecules, thereby facilitating diffusion into available adsorption sites. Similar temperature-dependent improvements have been reported for dye adsorption onto biomass-derived adsorbents and activated agricultural residues (Smoczyński *et al.*, 2020).

The increase in both adsorption capacity and removal efficiency further indicates that adsorption was not limited solely by external surface interactions but may also have involved diffusion into internal pores generated or enlarged during KOH activation. Elevated temperature may have improved accessibility to these internal adsorption sites, resulting in more effective dye uptake. Comparable observations have been reported for methyl red adsorption using activated biomass-derived adsorbents, where increased temperature enhanced dye diffusion and utilization of internal adsorption sites (Khalfaoui *et al.,* 2022).

Although both adsorbents benefited from increased temperature, orange peels displayed a more consistent response across all concentration levels. This suggests that the modified orange peel matrix possessed a more stable adsorption structure capable of sustaining efficient dye uptake under changing operational conditions. Consequently, 50 °C was identified as the optimum temperature for methyl red removal by both adsorbents.

3.7 Comparative Performance of Orange Peels and Moringa Leaves

A comparative assessment of the adsorption performance of KOH-modified orange peels and moringa leaves is presented in Table 7. Both adsorbents demonstrated appreciable capacity for methyl red removal; however, orange peels consistently exhibited superior overall performance. The maximum adsorption capacity achieved by orange peels was 2.386 mg g^{-1} with a corresponding removal efficiency of 95.43%, compared with 2.214 mg g^{-1} and 88.57% for moringa leaves. Orange peels also maintained more stable adsorption behaviour across variations in concentration, contact time, pH, and temperature, indicating greater operational robustness.

Table 7: Comparative performance of alkali-modified orange peels and moringa leaves for methyl red adsorption

Performance Indicator	Orange Peels	Moringa Leaves
pH_{pzc}	5.1	6.6
Maximum adsorption capacity, q_e (mg g^{-1})	2.386	2.214
Maximum removal efficiency (%)	95.43	88.57
Optimum pH	5	3
Optimum dosage (g)	0.1	0.1
Optimum contact time (min)	240	240
Optimum temperature (°C)	50	50

Although moringa leaves exhibited excellent performance under specific conditions, particularly at 8 mg L^{-1} dye concentration and under acidic conditions, their adsorption behaviour was generally more variable. The decline in adsorption capacity observed at higher dye concentration and increasing pH suggests greater sensitivity to changes in operating conditions. The superior performance of orange peels may be attributed to their lignocellulosic and pectin-rich composition, which provides abundant hydroxyl, carboxyl, and phenolic functional groups capable of interacting with dye molecules. Alkali modification may have further enhanced adsorption by increasing pore accessibility and exposing additional active sites. Similar advantages of citrus-derived biomass have been reported in several adsorption studies involving synthetic dyes and industrial wastewater treatment (Ramutshatsha-Makhwedzha *et al.*, 2022; Lawal and Abdulsalam, 2024).

From an application perspective, orange peels offer an additional advantage because they are widely available as an agricultural waste material and require minimal processing prior to utilization. The combination of availability, adsorption efficiency, and operational stability suggests that KOH-modified orange peels represent a more promising biosorbent for methyl red removal under the conditions investigated in this study.

3.8 Proposed Adsorption Mechanism

The adsorption behaviour observed in this study suggests that methyl red removal by KOH-modified orange peels and *Moringa oleifera* leaves occurred through a combination of physicochemical interactions rather than a single adsorption pathway (Figure 7). The effects of

DOI: https://doi.org/10.57233/ijsgs.v12i2.1114 ISSNp: 2488-9229; ISSNe: 3027-1118
IJSGS FUGUSAU VOL . 12(2) WEBSITE: https://fugus-ijsgs.com.ng

solution pH, contact time, initial dye concentration, adsorbent dosage, and temperature collectively provide insight into the adsorption mechanism operating in the present system. The strong dependence of adsorption performance on solution pH indicates that electrostatic interactions played a major role in methyl red uptake. Maximum adsorption occurred under acidic conditions, particularly at or below the pH_{pzc} of the adsorbents, where protonation of surface functional groups favoured attraction between the adsorbent surface and the anionic form of methyl red.

Hydrogen bonding likely also contributed to adsorption through interactions between hydroxyl and carboxyl groups present on the adsorbent surfaces and electron-rich oxygen and nitrogen atoms within the methyl red molecule. Furthermore, the improvement in adsorption capacity with increasing temperature suggests that adsorption was enhanced not only by surface interactions but also by increased diffusion of dye molecules into pores created or enlarged during KOH modification. The combined influence of these processes indicates that both surface adsorption and intraparticle diffusion contributed to dye removal.

The superior adsorption performance of orange peels relative to *Moringa oleifera* leaves is attributed to their lignocellulosic and pectin-rich structure, which provides a greater abundance of accessible hydroxyl and carboxyl functional groups together with a more favourable pore structure following alkali activation. Consequently, methyl red adsorption in the present study is best described as a physicochemical process governed by the simultaneous action of electrostatic attraction, hydrogen bonding, and pore diffusion. The relative contribution of each mechanism is expected to vary with operating conditions, particularly solution pH and temperature, but together these interactions adequately explain the adsorption behaviour observed for both biosorbents.

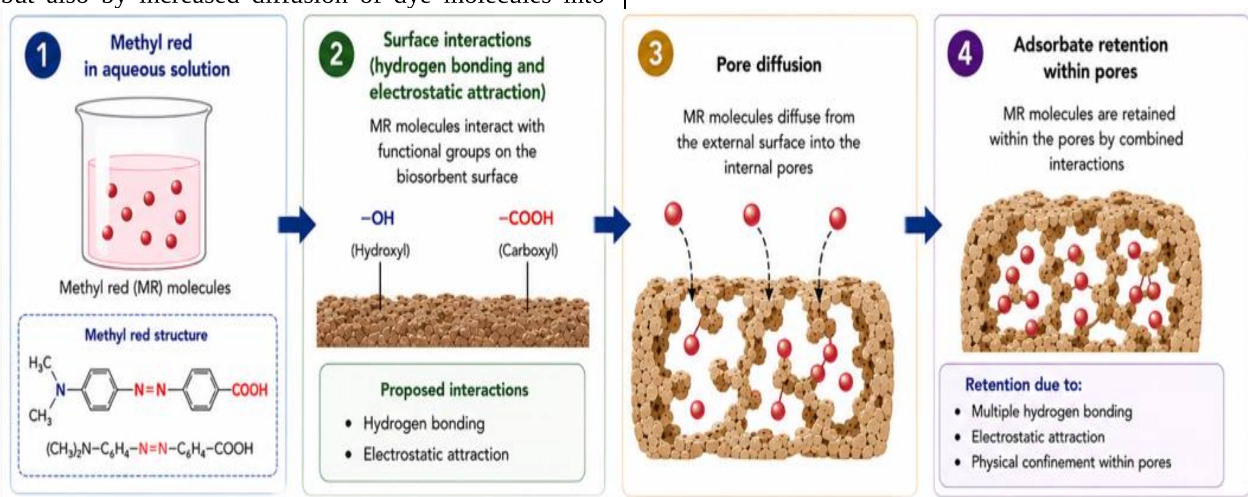

Figure 7: Conceptual representation of methyl red adsorption by alkali-modified orange peels and moringa leaves.

4.0 CONCLUSION

This study evaluated the adsorption performance of KOH-modified orange peels and moringa leaves for the removal of methyl red from aqueous solution under varying operational conditions.The adsorption behaviour of both biosorbents was strongly influenced by initial dye concentration, adsorbent dosage, contact time, solution pH, and temperature. The point of zero charge (pH_{pzc}) was determined as 5.1 for orange peels and 6.6 for moringa leaves, indicating differences in surface charge characteristics and adsorption behaviour. Adsorption capacity generally increased with increasing dye concentration, while percentage removal tended to decrease at higher concentrations due to progressive saturation of available adsorption sites. For both adsorbents, adsorption performance improved with increasing contact time up to an optimum of 240 min, beyond which no significant improvement was observed. Solution pH exerted a pronounced influence on methyl red removal. Maximum adsorption capacity was obtained at pH 5 for orange peels (2.386 mg g^{-1}; 95.43% removal) and at pH 3 for moringa leaves (2.214 mg g^{-1}; 88.57% removal), confirming the importance of surface charge interactions in the adsorption process. Increasing temperature from 40 °C to 50 °C generally enhanced adsorption performance, suggesting improved mobility of dye molecules and greater accessibility of adsorption sites.

A comparative evaluation showed that both biosorbents were effective for methyl red removal; however, KOH-modified orange peels consistently demonstrated superior adsorption performance, higher removal efficiency, and greater operational stability across the range of conditions investigated. The abundance of readily available functional groups and favourable surface characteristics of orange peels likely contributed to their enhanced adsorption behaviour. Overall, the findings demonstrate that alkali-modified orange peels and moringa leaves represent promising low-cost and environmentally sustainable biosorbents for dye-contaminated wastewater treatment. Among the two materials investigated, KOH-modified orange peels exhibited the greatest potential for practical application in methyl red removal systems.

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DOI: https://doi.org/10.57233/ijsgs.v12i2.1114 ISSNp: 2488-9229; ISSNe: 3027-1118

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Declaration:

Data Availability Statement: The datasets supporting the findings of this study are available in the manuscripts and further information can be made available on request.

Author(s) Contribution:

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Conflict of Interest: The authors declared no conflict of interest

Ethical Considerations: Not applicable

Funding: The author(s) declared no source of funding