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Removal of Methyl Orange from Aqueous Solution Using Orange Peel as a Low-Cost Adsorbent

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Abstract: The objective of this research was to evaluate the feasibility of using orange peels as a low-cost adsorbent to remove methyl orange (MO) from water solutions. The orange peel adsorbent underwent characterization through Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy to determine its properties before and after adsorption. A series of batch adsorption experiments were carried out to investigate the effects of various parameters such as contact time, adsorbent dosage, particle size, and initial dye concentration on the adsorption process. In each case, varying the value of the parameter of interest while keeping all other parameters constant. Results revealed that the highest removal of the dye from the adsorbent was achieved at a contact time of 90 min, the adsorbent dosage of 0.5 g, a particle size of less than 63 µm, and an initial concentration of 300 mg/L. Furthermore, the adsorption rate increased with increasing contact time, adsorbent dosage, and initial concentration, while it decreased with increasing particle size of the adsorbent. Concentrations of methyl orange were analyzed using a UV-Vis spectrophotometer. The experimental equilibrium data was analyzed using Langmuir and Freundlich isotherm models. The Langmuir isotherm provided the best fit for the experimental data with a correlation coefficient value of 0.9964 and a maximum adsorption capacity of 17.69 mg/g.

Keywords: Adsorbent, Orange Peel, Methyl Orange.

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1. INTRODUCTION

For a considerable period, water pollution has remained a critical issue. Pollutants like dyes, pesticides, and heavy metals have contributed to this problem (1). Water pollution presents significant hazards to both human beings and aquatic life (2). The textile sector is a significant contributor to water pollution. The wastewater generated from textile production facilities includes harmful dyes, which are carcinogenic and mutagenic (3).

Acid dyes are water-soluble anionic dyes that are typically applied to fibers. The majority of food dyes fall under the category of acid dyes. The azo group is the most prevalent chromophore found in acid dyes. Methyl orange, a commonly used water-soluble azo dye, serves as a pH indicator and is widely used in various industries, like the paper, textile, as well as food industries (4). Exposure to Methyl orange can result in symptoms such as vomiting and diarrhea, and high concentrations can lead to death.

There are several methods available for removing dyes from aqueous solutions, including coagulation-flocculation, biological treatment, chemical precipitation, electrochemical treatment, and adsorption (1,5). Adsorption is a highly desirable process, primarily due to its low operational cost, ease of operation, and lack of regeneration issues (6). In recent times, adsorption has become a widely used method in both industrial and environmental protection appli-cations. Undoubtedly, activated carbon is the most commonly utilized adsorbent for removing organic dyes due to its high adsorption activity and large surface area. However, in some countries, its usage is regulated because of its high cost and regeneration issues (5).

Low-cost adsorbents used in water treatment should exhibit qualities such as low economic cost, availability, and disposability without regeneration. Studies have examined the effectiveness of various low-cost materials, such as rice straw, orange peel, grain husk, banana peel, and biochar, in treating textile wastewater. These agricultural wastes are effective as low-cost adsorbents (7).

Materials such as orange peel, banana peel, coconut shell and other agricultural wastes have been reported as adsorbents in the removal of methyl orange from previous studies (2,7,10). Orange peel contains cellulose, hemicellulose, lignin, pectin, and chlorophyll pigments, which possess functional groups like hydroxyl and carboxyl groups. These components make orange peel a suitable adsorbent (8). OP is a viable adsorbent due to its cost-effectiveness, abundance, biodegradability, non-toxicity, and non-regeneration (9).

The objective of this study was to evaluate the efficacy of using orange peels, a natural waste material with no economic value, as an adsorbent for the removal of methyl orange from water. The study utilized unmodified orange peels as the adsorbent and conducted isotherm studies to determine their adsorption capacity. Orange peels are readily available in Nigeria and the study aimed to explore the potential of this abundant and underutilized waste material for water treatment purposes.

2. EXPERIMENTAL SECTION

2.1. Preparation of Adsorbent

Orange peels (*Citrus sinensis*) were obtained from local market vendors and cleaned to eliminate any physical impurities. After cleaning, the orange peels were dried for two days in the shade, and then finely ground using a mortar and pestle. The resulting powder was stored in sealed containers and labeled as "Orange Peel Adsorbent". Particle size of a portion of the ground OP was determined by using sieves of varying mesh sizes (<63 µm, 63-106 µm and 106-150 µm) to investigate the effect of particle size on adsorption of methyl orange.

2.2. Characterization of the Adsorbent

The morphological properties of the OP adsorbent were examined using a Scanning Electron Microscope (Phenom SEM PW-100-012) at 500× magnification, both before and after adsorption. The differences observed were discussed. In addition, Fourier Transmission Infrared (Cary 630 Agilent Technologies FT-IR) analysis was conducted on the OP adsorbent at a resolution of 8 cm^{-1} to identify the presence of certain functional groups.

2.3. Preparation of Adsorbate

The adsorption capacity of unmodified OP adsorbent was tested using analytical grade MO, which has a minimum absorption wavelength of 464 nm. To prepare the MO solution, 1 g of the dye was dissolved in 1 L of distilled water to create a stock solution with a concentration of 1000 mg/L. Working solutions with lower concentrations were made by diluting the stock solution using Equation 1.

$$C_1V_1 = C_2V_2 \quad \text{(Eq. 1)}$$

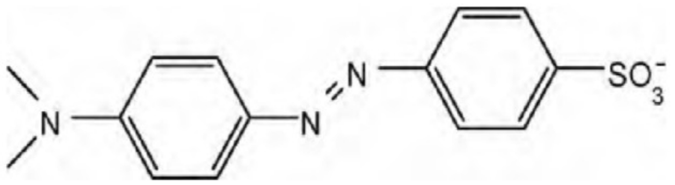

Figure 1: Structure of MO dye.

2.4. Batch Adsorption Experiment

Several experiments were conducted in a 100 cm^3 conical flask that contained 50 mL of methyl orange solution. Different parameters were taken into account, such as the contact time (30-90 min), the adsorbent dosage (0.1 – 0.5 g), the particle size of OP (<63 µm), and the initial concentration of the dye solution (300-1000 mg/L), while keeping other parameters constant. These parameters were selected in comparison with previous literatures (2,10), in order to explore the experimental reaction space which is expected to achieve the economic objective of this study. The experiments were performed at room temperature, and the mixture of methyl orange dye solution and unmodified OP adsorbent in a conical flask was sealed and agitated using a flask shaker (ST15 0SA – Barloworld) at 300 rpm. Samples were collected at specific contact times, filtered with Whatman filter paper (PW 184), and measured for the remaining dye amount using a UV/Vis Spectrophotometer at the maximum absorption wavelength of MO (464 nm). The removal efficiency of methyl orange was calculated using Equation 2.

$$\%\text{ removal}\left(\%R\right)=\frac{\left(C_0-C_t\right)}{C_0}\times 100\,\% \quad \text{(Eq. 2)}$$

Where C_0 is the initial concentration of the dye solution and C_t is the concentration at a particular time interval.

The amount of dye adsorbed per weight of OP adsorbent (adsorption capacity) can be calculated using Equation 3.

$$\text{Adsorption capacity}\left(q_e\right)=\frac{V\left(C_0-C_t\right)}{M} \quad \text{(Eq. 3)}$$

where C_0 is the initial concentration of the dye solution, C_t is the concentration at particular time intervals, V is the volume of adsorbate used and M is the mass of adsorbent used.

2.4.1. Adsorption Isotherms

The interaction between dye molecules and the surface of an adsorbent is described using isotherms (10). They show the relationship between the amount of dye adsorbed per unit weight of the adsorbent and the concentration of the dye in bulk at equilibrium (11). The two most commonly used isotherms are Langmuir and Freundlich isotherms. The Langmuir isotherm model assumes that adsorption occurs on a homogeneous surface composed of a single layer of adsorbent molecules (10). Equation 4 describes the Langmuir isotherm model.

$$C_e/q_e = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \text{(Eq. 4)}$$

where C_e is the concentration of methyl orange in solution at equilibrium (mg/L), q_e is the adsorption capacity of OP (mg/g), q_m is the maximum adsorption capacity of OP (mg/L) and K_L is a constant relating to adsorption heat (L/mg) (12).

A linear plot of C_e / q_e against C_e can be used to determine the values of K_L and q_m (10). The R_L value is a parameter used to evaluate the favorability of the Langmuir model and is calculated using Equation 5. If $R_L>1$, the adsorption process is unfavorable, if $R_L=1$, it is considered to be a linear process, if $0<R_L<1$, it is favorable, and if $R_L=0$, the process is considered to be irreversible.

$$R_L = \frac{1}{(1+K_L C_o)} \qquad \text{(Eq. 5)}$$

where K_L is the constant relating to adsorption heat and C_o is the initial concentration.

While the linear form of the Freundlich isotherm is given by Equation 6.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad \text{(Eq. 6)}$$

where C_e is the concentration of methyl orange in solution at equilibrium (mg/L), q_e is the adsorption capacity of OP (mg/g), K_f is a constant relating to adsorption capacity and n is a constant relating to adsorption intensity (12). A linear plot of ln q_e against ln C_e can be used to determine the values of K_f and n (10).

3. RESULTS AND DISCUSSION

3.1. Characterization

The adsorbent's surface morphology is depicted in Figure 2 representing the condition after adsorption. The observation revealed that the adsorbent possesses clustered pores of various particle sizes after the adsorption experiment (13,14). The presence of pores increase the number of adsorption sites. Figure 2a shows that OP exhibits a uniform dispersion of vacant sites before adsorption while Figure 2b indicates shrinkage of the adsorption sites. It was further observed that the pore size reduced and became more uniform. This change was attributed to the filling up of the pores by methyl orange molecules, leading to particle aggregation, potential liquid bridge, and compaction within the pores of the orange peel adsorbent. This further confirms the presence of occurring adsorption on the adsorbent.

Figures 3 and 4 present the FT-IR spectrum of the adsorbent before and after adsorption respectively. The peak observed at 3324 cm^{-1} indicated the presence of the OH functional group, while the peak at 2921 cm^{-1} indicated the presence of C-H stretching vibrations. The peak observed at 1607 cm^{-1} indicated the presence of conjugated C=C bonds. The peak at 1737 cm^{-1} indicated the presence of carbonyl groups, such as esters, aldehyde, ketones, or carboxylic acid groups. The presence of carbonyl groups, such as esters, aldehyde, ketones, or carboxylic acid groups, is indicated by the peak at 1737 cm^{-1}. The peaks detected at 1369 cm^{-1} represented $-CH_2-$ and $-CH_3$ bending vibrations. The results indicated the presence of cellulose, hemicellulose, and lignin. More peaks were detected in the fingerprint region after adsorption, as shown in Figure 5. This could be attributed to the presence of adsorbed methyl orange molecules. A slight shift in the wave number of the OH peak was observed, from 3324 cm^{-1} to 3387 cm^{-1}. This demonstrated the active involvement of the OH group in the adsorption process.

3.2. Effect of Contact Time

Batch adsorption experiments were conducted at room temperature, utilizing an adsorbent dosage of 0.5 g / 50 mL, an initial dye concentration of 0.5 g/L, and varying contact times of 30 min, 60 min, and 90 min, as shown in Figure 5. The results indicated that as the contact time increased, the percentage removal and adsorption capacity also increased. At a contact time of 30 min, the percentage removal of the dye was 24% and the adsorption capacity was 12 mg/g. This increased to 36% percentage removal and 16 mg/g adsorption capacity at a contact time of 60 mins. At a contact time of 90 minutes, the percentage removal further increased to 44% and the adsorption capacity increased to 22 mg/g. The increased time from 30 to 60 min suggests a 50% increment in OP removal whereas a 22% increment was noted between 60 min to 90 min. The steep increase from 60 min to 90 min is evidence of saturation of the pore sites by the OP which resulted in potential liquid bridging as noted by the SEM findings. In addition, the findings are consistent with the increased adsorption capacity as shown in Figure 5. Previous findings align with the results reported herein (15,16).

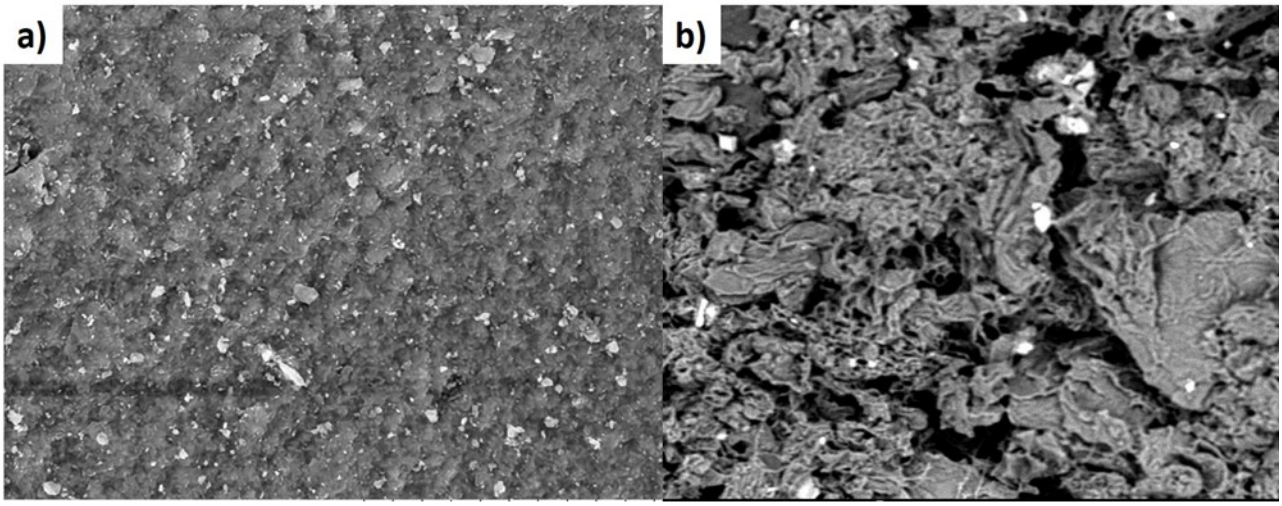

Figure 2: SEM Image of OP a) before b) after adsorption.

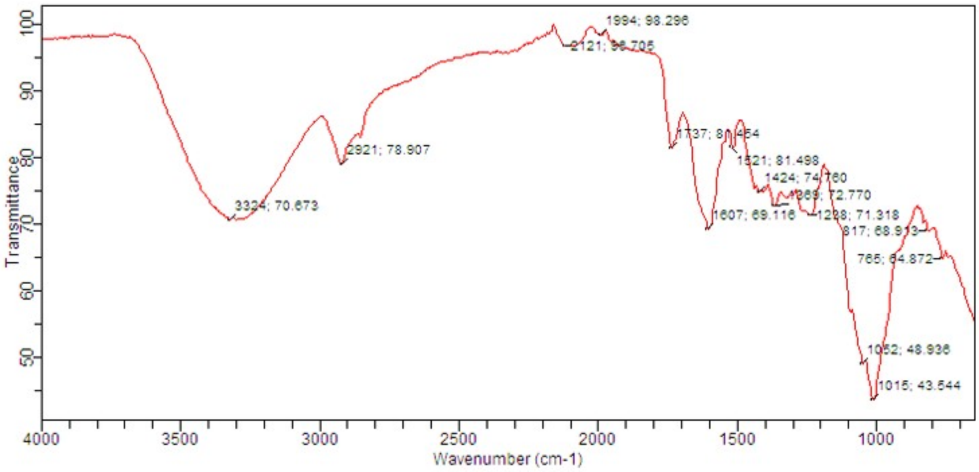

Figure 3: FT-IR spectrum of OP before adsorption.

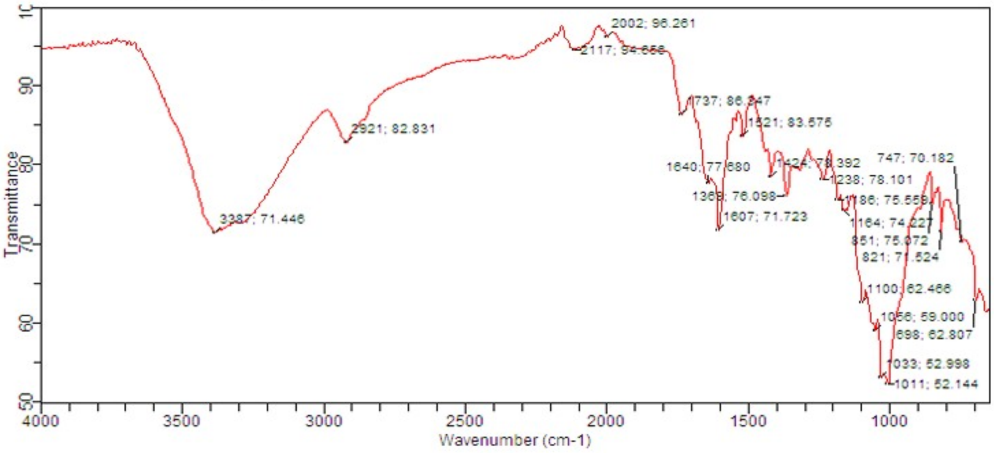

Figure 4: FT-IR spectrum of OP after adsorption.

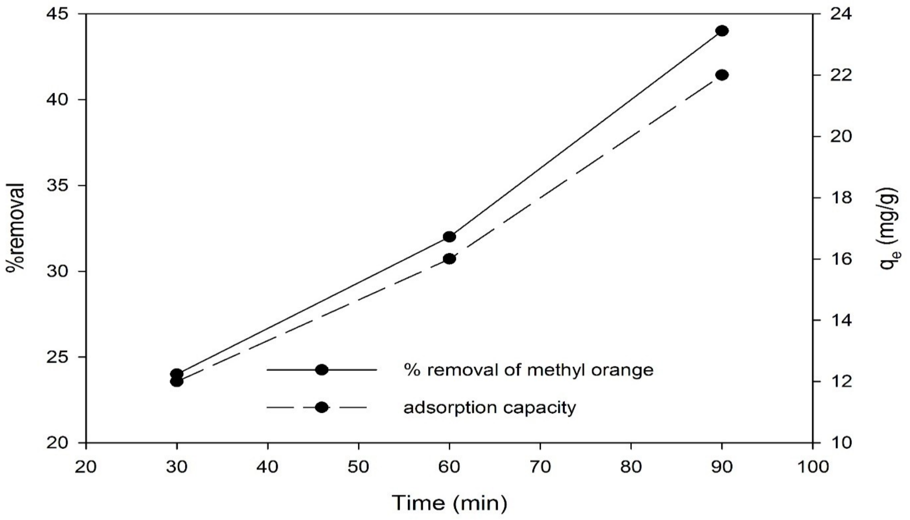

Figure 5: Effect of contact time on % removal.

3.3. Effect of Adsorbent Dose

The effect of the adsorbent dose was investigated by varying the amount of adsorbent (0.1 g, 0.3 g, and 0.5 g) as shown in Figure 6 and keeping all other parameters constant: initial concentration of dye solution (500 mg/L), contact time (30 min) and room temperature (17). It was discovered that there is an increase in percentage removal with an increase in adsorbent dose. It was also observed that as the adsorbent dose increased from 0.1 – 0.3 g the percentage removal increased from 4-16% and the adsorption capacity increased from 2 mg/g to 8 mg/g. Upon increase of the adsorbent dose from 0.3 – 0.5 g the percentage removal increased from 16% to 24% and the adsorption capacity increased from 8 mg/g to 12 mg/g. This observation is attributed to increased adsorption sites and surface area of the adsorbent which in turn provides additional vacancy for adsorbate take up (18).

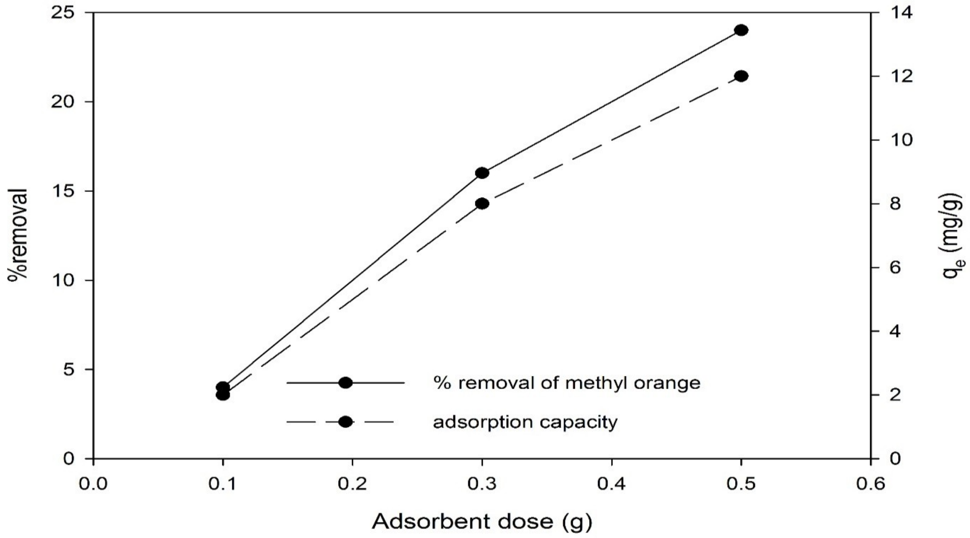

Figure 6: Effect of adsorbent dose on % removal.

3.4. Effect of Initial Concentration

Three different concentrations (300 mg/L, 600 mg/L, and 1000 mg/L) of methyl orange were used to investigate the effect of initial concentration on the percentage removal at constant values of adsorbent dosage (0.5 g / 50 mL), contact time (30 min), and at room temperature. As observed in Figure 7 as the concentration increases, the adsorption capacity also increases due to higher competition of methyl orange molecules on the OP at higher concentrations. On the other hand, the % removal decreases as the initial concentration is increased. During the experiment, all other parameters were kept constant. This observation agrees with the results from the work on the adsorption of methyl orange using a lala clamshell (10). At the initial concentration of 300 mg/L, the percentage removal was 40% and the amount of methyl orange adsorbed was 12 mg/g, at the initial concentration of 600 mg/L, the percentage removal decreased to 23.3% and the amount of methyl orange adsorbed increased to 14 mg/g and at the initial concentration of 1000 mg/L, the percentage removal further decreased to 16% but the amount of dye adsorbed increased to 16 mg/g. The observed decreasing trend of % removal can be attributed to the saturation of adsorption sites on the OP at higher concentrations. The availability of unoccupied sites becomes limited for the adsorption of the methyl orange molecules to occur effectively (19).

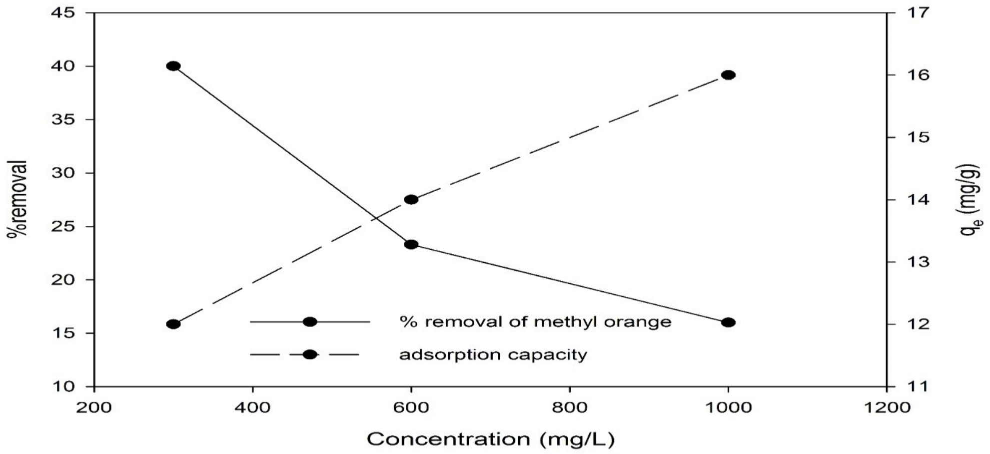

Figure 7: Effect of initial concentration on % removal.

3.5. Effect of Particle Size

The effect of the size of the adsorbent was investigated using three different sizes of OP adsorbent (<63 µm, 63-106 µm, and 106-150 µm) while other parameters were kept constant: 0.5 g / 50mL adsorbent dose, 30 min contact time and at room temperature. It was observed that % removal and adsorption capacity increases as the size of the adsorbent decreases. A significant inc-rease in the % removal and adsorption capacity was recorded between 63-106 µm and <63 µm as shown in Figure 8. Between particle sizes of 106-150 µm and 63-106 µm, % removal increased from 20% to 24% while adsorption capacity increased from 10mg/g to 12 mg/g and between particle sizes of 63-106 µm and <63 µm, % removal increased from 24% to 36% while adsorption capacity increased from 12 mg/g to 18 mg/g. The higher removal of methyl orange observed on the smallest particle size (<63 µm) can be linked to the rapid diffusion rate of methyl orange in and out of the OP adsorbent. In addition, the path length is shortened which exposes the pores to the methyl orange and is expected to eliminate the influence of intraparticle diffusion resistance. The result obtained agrees with similar research (7).

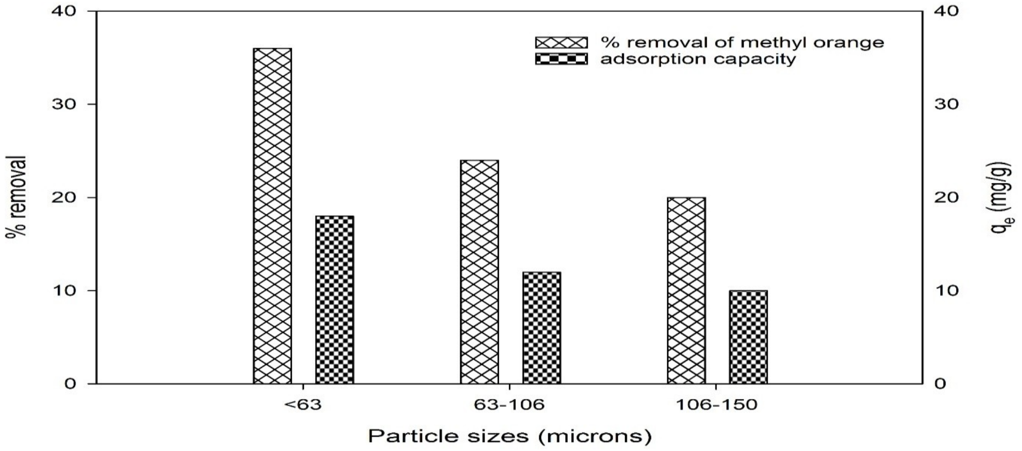

Figure 8: Effect of particle size on % removal.

3.6. Adsorption Isotherms

The results from the experiments were studied using isotherm models. It was studied at different initial concentrations (300 mg/L, 600 mg/L, and 1000 mg/L) of the methyl orange solution, contact time of 30 min, 0.5 g / 50 mL adsorbent dose, and room temperature. The distribution and interaction of dyes on the surface of the adsorbent are illustrated using adsorption isotherm models (20). The two most used isotherm models are Langmuir and Freundlich isotherm models as shown in Tables 1 and 2. The experiment best fitted the Langmuir isotherm model producing a straight line graph and a higher R^2 value of 0.9964 as illustrated in Figure 9. The calculated q_m was 17.69 mg/g which is not far from the value obtained by the experiment which is 16 mg/g. Therefore, Langmuir isotherm is favorable for the adsorption of methyl orange onto orange peel. R_L value shows the nature of the adsorption process to be unfavorable if $R_L>1$, linear if $R_L = 1$, favorable if $0<R_L<1$, or irreversible if $R_L = 0$. The R_L value 0.0893 was obtained which falls in the range $0 < R_L< 1$. This further ascertains that the experiment was better fitted by Langmuir isotherm.

Table 1: Langmuir isotherm constants for adsorption of methyl orange onto orange peel.

q_m (mg/g)	K_L(L/mg)	R^2	R_L
17.69	0.0102	0.9964	0.0893

Table 2: Freundlich isotherm constants for adsorption of methyl orange onto orange peel.

K_f(mg/g)	N	R^2
4.4916	5.3333	0.9955

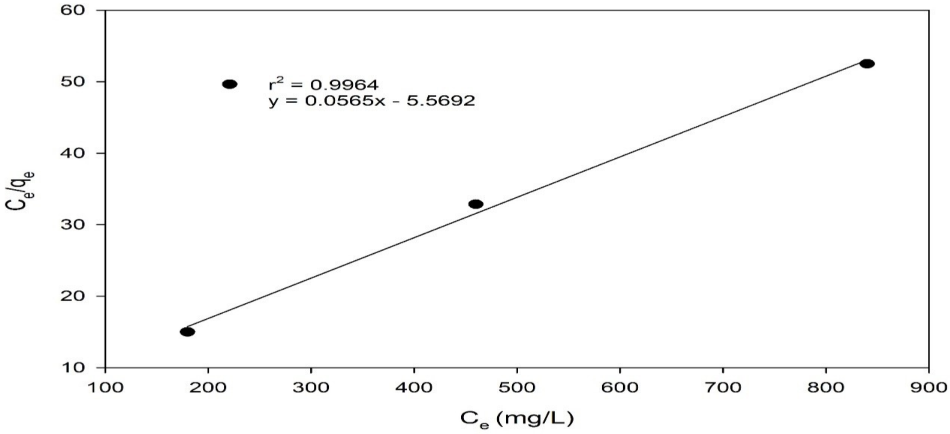

Figure 9: Langmuir isotherm curve.

4. CONCLUSION

The Experimental results showed that orange peel can be used as a low-cost adsorbent for the removal of methyl orange. It was observed that an increase in the reaction parameters showed an increasing trend for the removal of dye except for increased concentration which is due to saturation of adsorption sites. Scanning electron microscope analysis showed the aggregation of particles after adsorption. FT-IR analysis showed the presence of OH, C=O, and C=C conjugated bonds and showed that OH participated actively in the adsorption process. The adsorption experiment in this study was favored by the Langmuir isotherm model with an r^2 of 0.9964. It is concluded that orange peel is a favorable low-cost adsorbent due to its availability.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

6. ACKNOWLEDGMENTS

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