The investigation revealed that the adsorption capacity of the powdered ceramics on the removal of methyl orange dye is high enough compared to observed values in literatures. Freundlich's model fitted the equilibrium data better, while the pseudo-second-order kinetic model was the most fitting from the kinetic data obtained for the adsorption of methyl orange dye.

Conclusion: The investigation revealed that the adsorption capacity of the powdered ceramics on the removal of methyl orange dye is high enough compared to observed values in literatures. Freundlich's model fitted the equilibrium data better, while the pseudo-second-order kinetic model was the most fitting from the kinetic data obtained for the adsorption of methyl orange dye.

Keywords: Ceramics, Methyl orange, Dye, Pollutants, Adsorbent, Adsorption

INTRODUCTION

Dyes can be defined as substances that are intensely coloured, soluble giving transparent solutions and can be applied in solution or dispersion to fabrics or surfaces to give coloured materials considerable fastness [1]. Dyes can be classified depending on their origin as natural and synthetic dyes. Natural dyes are got from nature, that is, vegetable matter, insects and minerals while synthetic dyes are gotten during synthesis, which results in the formation of dyes as a byproduct. Dyes can be classified as synthetic and natural dyes. Dyes usually have a synthetic and complex aromatic molecular structure, which makes them to be stable and difficult to biodegrade. Each dye has particular effects they cause to the living organism that are exposed to them. For example, Azo-dyes undergo biological and photochemical degradation when they reach the aquatic environment. The degradation products are more harmful and persistent than the parent compound [14].

The presence of dye in water affects the photosynthetic activity in aquatic life by reducing light penetration, which serves as source of energy to most aquatic organisms [15]. It causes depletion of dissolved oxygen (DO), which implies that there will be increase in the chemical oxygen demand (COD) and biological oxygen demand (BOD) that refers to the amount of oxygen required to completely oxidize the organic substances in water chemically and biologically respectively. The depletion of dissolved oxygen (DO) makes the anoxic bacteria to take over which leads to formation of CH$_4$, H$_2$S and NH$_3$ [16]. These products formed are toxic to aquatic organisms and human that consumes the fish that accumulates it. The elimination of the dye-stuff content from the effluent is done mostly by conventional methods, which include physico-chemical methods--a methods that joins both physical and chemical means of separating dyes from the effluent, such as ion flotation, solvent sublimation, and electrocoagulation. Another conventional method is photo-catalysis and oxidation methods. Commercial dyes have high resistance to photo-degradation, which has led to the development of catalysts and oxidizing agents for decolourization of dye wastewater. The catalysts and oxidizing agents such as hydrogen peroxide with iron (III) and ozone were reported effective in degradation of the dye intermediate anthraquinone-2-sulphonic acid sodium salt [17] and decolouration of orange (II), oxalate, formate and benzene sulphonate ions were the most important decomposition products [18, 19] respectively.

Methyl orange (MO) was selected as the adsorbate in this adsorption studies, representing anionic organic pollutants as they are easy to be analyzed by UV-VIS Spectrophotometry. Methyl orange (Sodium 4-[(4-dimethylamino)phenylidiazetyl]benzenesulphonate) is a water-soluble, anionic, azo-dye with the molecular formula C$_{14}$H$_{14}$N$_3$O$_3$SNa and molecular weight of 327.33 (g/mol) [20].
However, the aim of this study was to assess and evaluate the efficiency of crushed ceramics in adsorbing methyl orange dye from aqueous solutions while determining the optimum operating parameters for the process.

**MATERIALS AND METHODS**

All chemicals and reagents were of analytical grade.

**Adsorbent preparation**

Ceramics was purchased from Oja-Oba market in Akure, Ondo State, Nigeria, crushed with grinding stone, and sun-dried for two days. The dried-crushed ceramics was then sieved with 63 µm laboratory test sieve to produce homogenized particle size (fig. 1) and stored in an air-tight container until usage.

![Crushed ceramic adsorbent](image)

**Preparation of methyl orange dye stock solution**

100 mg/l of methyl orange dye solution was prepared by adding 100 ml of the standard solution of methyl orange dye stock in 1000 ml standard flask and added up to the mark with distilled water.

**Preparation of working standard solutions for UV-visible spectrophotometer**

Ten working solutions were prepared from the stock solution using the dilution formula:

\[ C_1V_1 = C_2V_2 \]

Where \( C_1 \) is the concentration of the standard solution (100 mg/l), \( V_1 \) is the required volume of the standard, \( C_2 \) is the required working standard concentrations (10 mg/l to 100 mg/l) and \( V_2 \) is 10 ml.

**Determination of effect of pH**

To test for the effect pH on the adsorption process, 1.0 g of the adsorbent was weighed into 7 pre-labeled beakers, and 25 ml of 100 mg/l of methyl orange dye solution were added into each beaker. Thereafter, the pH of the mixtures was adjusted to 1.0, 2.0, 3.0, 4.5, 6.0, 7.0 and 8.0 for the seven beakers, respectively, using 0.1M HCl and 0.1M NaOH solutions. After that, the samples were agitated using orbital shaker at 100 rpm for 15 min. The samples were withdrawn from the shaker after this period, centrifuged, and the dye solution was separated from the adsorbent by decantation. The absorbance of the supernatant solution was measured using UV-VIS Spectrophotometer at wavelength 464 nm [21].

**Determination of effect of contact time**

The beakers to be used were labeled, and 1.0 g of the adsorbent was weighed into 10 beakers, after which 25 ml of 100 mg/l Methyl orange dye solution were added into each beaker. After this, each sample was adjusted to the optimum pH, and the samples were shaken on the orbital shaker at different time interval. The time intervals used, in minutes, were: 2, 5, 10, 15, 20, 25, 30, 60, 90 and 120. Each sample was withdrawn at each time interval, centrifuged, and the dye solution was separated from the adsorbent by decantation. The absorbance of supernatant solution was measured using UV-VIS Spectrophotometer at wavelength 464 nm [21].

**Determination of effect of adsorbent dosage**

The beakers were labeled, and different adsorbent dosages (0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 g) were weighed into them, respectively. Thereafter, 25 ml of 100 mg/l Methyl Orange dye solution were added to each sample in the beaker. After this, each sample was adjusted to the optimum pH and agitated. The samples were withdrawn from the shaker after the optimum contact time, centrifuged and the dye solution was separated from the adsorbent by decantation. The absorbance of supernatant solution was measured using UV-VIS Spectrophotometer at wavelength 464 nm [21].

**Determination of effect of initial concentration**

1.0 g of the crushed ceramic adsorbent was weighed into the labeled beakers. Thereafter, 20 ml of different initial dye concentrations of 50, 100, 150, 200, 250 and 300 mg/l were pipetted into pre-labeled beakers. After this, the samples were adjusted to the optimum pH and agitated. The samples were withdrawn from the shaker after the optimum contact time, centrifuged and the dye solution was separated from the adsorbent by decantation. The absorbance of the supernatant solution was measured using UV-VIS Spectrophotometer at wavelength 464 nm [21].

**Determination of the effect of temperature**

The crushed ceramic adsorbent 1.0 g was weighed into the labeled beakers. Thereafter, 20 ml of 50 mg/l of methyl orange dye solution were added respectively into each beaker at room temperature, 35, 45, 55 and 65 °C by batch experiments, at constant pH and were shaken on the water bath shaker for the same contact time. The supernatant was collected after centrifugation and decantation; and measured using UV-VIS
Spectrophotometer at wavelength 464 nm [21]. This procedure was repeated for 100, 150, 200, 250 and 300 mg/l of dye solution, respectively for the elucidation of the kinetic characteristics of the adsorption.

Statistical analysis

All the experiments were conducted in duplicates and the data were presented as mean values, standard deviation of the duplicate determinations, and as graphs and curves using Microsoft Excel, 2016.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Fig. 2 and 3 show the FTIR spectra of the adsorbent before and after adsorption. The two spectra show similar peaks, with the second spectra having a slight shift to the left. The peak at 3649.1 cm⁻¹ in the before-spectra was due to the stretching of O-H group as a result of intermolecular and intra-molecular hydrogen bonding of polymeric compounds such as alcohols or pectin, hemicelluloses, cellulose and lignin [22]. The peak around 2940.9 cm⁻¹ in the after-spectra corresponds to the stretching vibrations of C-H bond of methyl (CH₃), methylene (=CH₂), methoxy group (OCH₃). The intense peak at 1051.1 cm⁻¹ corresponded to the C-O stretching of alcohol or carboxylic acid [23].

The peak at 775 cm⁻¹ corresponds to the C-H stretching in the aromatic ring [24].

Optimization of factors affecting the adsorption of methyl orange on crushed ceramics

Effect of pH

The effect of pH on the removal of methyl orange in a solution by crushed ceramics adsorbent was studied at pH of 2 to 8. Fig. 4 below shows the removal efficiency (%) with their corresponding pH values.

The removal efficiency (%) of methyl orange by the adsorbent was generally higher at the lower pHs of 1 (98.29%) and 2 (99.31%) compared to the other pHs. This may be due to the fact that at lower pH, the surface of the adsorbent becomes more protonated, having more H⁺ from the 0.1M HCl and other positive ions that may be there as impurities. This in turn makes methyl orange dye, which is an anionic dye, bind with the surface of the adsorbent easily. With an increase in pH, the hydroxyl ion (OH⁻) from the 0.1M NaOH competes with the anionic dye for sorption sites, thereby reducing its adsorption efficiency [25]. Dye removal has been reported to be dependent on physicochemical property such as pH [26].
Effect of pH

The optimum pH for the rest of the experiments was thus selected as pH 2 with a removal efficiency of 99.31% and was chosen as one of the parameters in the next optimization factors.

Effect of contact time

Contact time plays a key role in the adsorption process and it often determines the amount of dyes adsorbed on an adsorbent. It is an important parameter for successful use of the adsorbents for practical applications. Rapid adsorption is among the desirable parameters in choice of a suitable adsorbent. The effect of contact time on the adsorption of methyl orange dye was investigated and the results are displayed in fig. 5 below.

As shown in the fig. 5, the rate of sorption of methyl orange dye generally increases with increasing the contact time. At 90 min, the equilibrium is achieved as a result of the binding sites that became exhausted. The percentage removal gradually slowed down due to decreasing availability of active sites by Methyl orange [27].

Effect of adsorbent dosages

The effect of adsorbent dosages ranged from 0.1 g to 2.5 g on the adsorption of methyl orange is presented in fig. 6.

As it can be seen from fig. 7, adsorption of the Methyl orange dye increased from 89% to 94% with increase in adsorbent dosage from 0.1 to 1 g. At adsorbent dosage of 2 g, the percentage removal dropped, which was as a result of the overlapping of the adsorption sites.

The results show that as the adsorbent dosage increases the affinity for methyl orange to bind with the binding sites decreased which was observed to be due to the overlapping of the negatively charged ions at the surface of the adsorbent [28]. An increase in the adsorbent dosage later increased with the percentage removal and reached its equilibrium again at 2.5 g with % removal 91%, which was as result of the binding sites available have become exhausted.
Effect of the initial concentration

The effect of the initial concentration ranges from 50, 100, 150, 200, 250 and 300 mg/l on the amount of methyl orange adsorbed is presented in fig. 7.

Fig. 6: Effect of the adsorbent dosage on removal of methyl orange dye. pH = 2.0, Initial concentration = 100 mg/l, Agitation speed = 100 rpm, Contact time = 90 min, data is expressed as a mean of triplicate

Fig. 7: Effect of the initial concentration on removal of Methyl orange. pH = 2.0, Agitation speed = 100 rpm, Contact time = 90 min, Adsorbent dosage = 1.0 g. Data is expressed as a mean of triplicate

Fig. 8: Effect of temperature on removal of methyl orange dyes, Eriochrome Black T and their binary mixture using untreated pulverized elephant grass. pH = 2.0, Agitation speed = 100 rpm, Contact time = 90 min, Initial concentration = 30 mg/l, Adsorbent dosage = 1.0 g. Data is expressed as a mean of triplicate
It was observed in fig. 8 that with increase in the initial Congo red concentration, the percentage removal first increased then decreased. The percentage removal decreased because at higher concentration the available sites on the adsorbent become limited. The adsorption capacity increased as dye concentration increase as a result of utilizing all available adsorption sites at higher concentration [29]. Previously, physicochemical property such as initial dye concentration has been shown as a key factor in dye removal [26].

**Effect of temperature**

Fig. 8 shows the effect of temperature on the adsorption efficiency.

**Adsorption isotherms**

**Langmuir's adsorption isotherm**

The Langmuir's isotherm model is a straight-line graph which is a plot of $C_e/q_e$ against $C_e$. For the sorption of methyl orange onto crushed ceramic adsorbent, the Langmuir's isotherm model graph was presented in fig. 9.

![Langmuir's isotherm for methyl orange adsorption](image)

**Table 1: Langmuir's isotherm parameters**

<table>
<thead>
<tr>
<th>Methyl orange</th>
<th>$Q_{max}$</th>
<th>$K_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>22.31</td>
<td>0.020</td>
</tr>
</tbody>
</table>

**Table 2: $R_L$ values for the adsorption of methyl orange mixture**

<table>
<thead>
<tr>
<th>Methyl orange</th>
<th>Initial Concentration</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>50</td>
<td>0.49</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>100</td>
<td>0.41</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>150</td>
<td>0.35</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>200</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Freundlich's adsorption isotherm**

The Freundlich’s isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed [30].

The Freundlich’s model was expressed as:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad \ldots \ldots \ldots (1)$$

Freundlich's isotherm model is a straight-line graph and a plot of $\log q_e$ against $\log C_e$. For the sorption of methyl orange onto crushed ceramic adsorbent, the Freundlich's isotherm model graph was presented in fig. 10.
Results obtained show that the equilibrium data for the adsorption of methyl orange are best fitted for Freundlich's isotherm because the N-value and their R² values are close to one. Chen et al. [31], however, proposed that the values of N in the range of 2 to 10 are good, 1 to 2 values are moderate and less than 1 are poor sorption characteristics. For the sorption of methyl orange, the multi-layer is formed, which is the physico-sorption type of adsorption.

**Adsorption kinetics**

Adsorption kinetics provides information about the mechanism of adsorption, which is important for the efficiency of the adsorption process.

**Pseudo first-order model**

This is the plot of log (q_t - q_e) against time in which K_1 and q_e are calculated from the slope and intercept, respectively from the plot. Fig. 11 shows the plot of pseudo first order model at a concentration of 100 mg/l and at varied time (10, 15, 20, 25 min).
Table 4: Pseudo-first-order kinetic parameters for methyl orange

<table>
<thead>
<tr>
<th>q-exp (mg/g)</th>
<th>Methyl orange</th>
</tr>
</thead>
<tbody>
<tr>
<td>q-cal (mg/g)</td>
<td>K1 (min⁻¹)</td>
</tr>
<tr>
<td>76.87</td>
<td>84.92</td>
</tr>
</tbody>
</table>

Pseudo second-order model

The pseudo-second-order kinetic rate equation was expressed as [32]:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \ldots \ldots \ldots (1)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e} \quad \ldots \ldots \ldots \ldots (2)
\]

This is the plot of t/q against time in which q_e and k_2 are calculated from the slope and intercept, respectively, from the plot. Fig. 12 shows the plot of pseudo second order model at a concentration of 100 mg/l and at varied time (10, 15, 20, 25 min).

![Graph](image)

Fig. 12: Plot of pseudo second order model of the adsorption of methyl orange on crushed ceramic pH = 2.0, Initial concentration = 100 mg/l, Agitation speed = 100 rpm

Table 5: Pseudo second order kinetic parameters for the adsorption of mercury (II) ions, Congo red dye and their binary mixture by modified mango leaves

<table>
<thead>
<tr>
<th>q-exp (mg/g)</th>
<th>Methyl orange</th>
</tr>
</thead>
<tbody>
<tr>
<td>q-cal (mg/g)</td>
<td>K1 (min⁻¹)</td>
</tr>
<tr>
<td>-0.0017</td>
<td>45.455</td>
</tr>
</tbody>
</table>

By comparing table 4 and 5, Pseudo Second Order kinetics was seen as the best fitted for the adsorption of methyl orange onto crushed ceramics than Pseudo First Order kinetics since the calculated equilibrium adsorption capacity value of methyl orange was close to the experimental equilibrium adsorption capacity value in Pseudo Second Order kinetics than in Pseudo First Order kinetics.

CONCLUSION

In this study, powdered ceramics were investigated for their performances in removing methyl orange from contaminated aqueous solutions. FTIR spectra of ceramics powder revealed that OH, C-H, C=C, C-O stretching were responsible for the adsorption. Effects of the different experimental parameters that influenced the efficiencies of the adsorbent have been evaluated and optimized.

Since wastewater from the textile and dye industries contain a lot of coloured organic compounds, this work was geared towards removing methyl orange dye at once from the contaminated aqueous solutions. The investigation revealed that the adsorption capacity of the powdered ceramics on removal of methyl orange dye is high enough to be comparable to observed values in literature. Kinetic data obtained for the adsorption of methyl orange dye was fitted well with pseudo second order model.

It can be concluded that crushed ceramics can be considered as an alternative sorbent for the removal of the dye since it is effective, low-cost, and abundant and can be obtained locally. The results showed that pulverized ceramics have the potential to be applied as alternative low-cost sorbent in the remediation of colour contamination in wastewater.

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AUTHORS CONTRIBUTIONS

OTF conceived the idea for this research and proposed the design. OTF, OOJ and JM conducted the experiments, carried out analysis and discussion of the results. OTF drafted the original writing of this work while OOJ carried out a critical review on revised manuscripts. JM carried out a proofreading and editing of the manuscript. All authors read and approved the final manuscript.

CONFICT OF INTERESTS

Authors declare no competing interest. All authors give their consent to the publication of this research article.

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