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Sustainable Remediation of Synthetic Azo Dyes: Enhanced Adsorption Performance of Titanium Dioxide-Modified Kaolin Clay in Wastewater Treatment

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Abstract

This study aims to assess the effectiveness of both activated and inactivated clay in removing synthetic azo dyes from industrial wastewater. Due to their toxicity and persistence, dyes such as Congo Red, Sudan Black, Methyl Orange, and Methylene Blue pose serious environmental threats. Conventional treatment methods are often costly and unsustainable, making it necessary to explore more affordable and eco-friendly alternatives. This research investigates the adsorption potential of kaolin clay under different conditions, including variations in adsorbent dosage, contact time, pH, temperature, and initial dye concentration. Furthermore, the study examines adsorption kinetics and thermodynamic behavior to gain a deeper understanding of the mechanisms involved in dye removal. To achieve this, the clay adsorbent was characterized using analytical techniques such as X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDX) to determine its structural, chemical, and physical properties. Batch adsorption experiments were conducted to evaluate dye removal efficiency. The adsorption process was analyzed using kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. Additionally, thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy were assessed to determine the feasibility and spontaneity of adsorption. The effects of key factors such as adsorbent dosage (0.5g–2.5g), pH (2–11), contact time (30–75 minutes), temperature (30°C–70°C), and dye concentration (50–150 mg/L) were examined to optimize adsorption conditions.

The results demonstrate that both kaolin with titanium dioxide and plain kaolin effectively remove dyes, with activated clay exhibiting superior adsorption performance due to its increased surface area and porosity. The adsorption process follows pseudo-second-order kinetics, indicating that chemisorption is the primary mechanism. Isotherm studies suggest monolayer adsorption, with the Langmuir and Freundlich models providing insights into adsorption capacity and surface heterogeneity. Thermodynamic analysis confirms that adsorption is spontaneous and exothermic, with higher efficiency at lower temperatures. These findings highlight the potential of clay as an inexpensive and sustainable solution for treating dye-contaminated wastewater, offering a practical alternative to conventional treatment methods.

Keywords: kaolin clay, titanium dioxide, adsorption, mixed azo dyes, wastewater treatment, pseudo-second-order kinetics, Freundlich isotherm, chemisorption, sustainable remediation, dye removal.

INTRODUCTION

One of the most significant and prevalent elements in the environment is water. Water is essential to the life and flourishing of all living things on Earth. Currently, the only planet with almost 70% water is Earth. However, it is heavily contaminated with many dangerous pollutants as a result of the growing human population, industrialization, fertilizer usage in agriculture, and human activities. Because the human population contracts a variety of water-borne illnesses as a result of drinking water contamination, it is essential that the quality of drinking water be monitored on a regular basis. Since the chemistry of water reveals a lot about the ecosystem's metabolism and explains the general hydro-biological relationship, it is challenging to fully comprehend the biological phenomenon (Basavaraja simpi et al 2011).

Water is very necessary for life to exist, but it also greatly improves our quality of life. Numerous studies have shown the direct and indirect harmful effects of heavy metals on skin allergies, malignancies, and tumors. Water is also crucial for enhancing quality of life. In 2021, Parvatham et al. Many attempts are made to provide alternatives to the issues brought on by excessive water usage, and one of the most well-known solutions is wastewater treatment and reuse. Kitchenette wastewater, cleaning water, and washing and rinsing water are all combined to create the massive wastewater, which has a very high concentration of organic materials including protein, carbohydrates, and fats. Many techniques are used to treat wastewater, and in this study, an attempt was made to investigate the use of inexpensive adsorbents by treating the wastewater by adsorption with activated clay.

A crucial process that involves the addition of a coagulant, coagulation destabilizes and neutralizes suspended particles, causing them to form big flocs or aggregates. Because of ion adsorption and surface group ionization, negatively charged suspended particles usually aggregate with positively charged coagulant. (Rathilal, 2021)

When pollutants and pathogens are present in excess of a certain threshold, water pollution results. The majority of pollution is brought on by human activity, including sewage emissions, wastewater, and garbage from homes and businesses, metals and particulate matter from mining and metallurgy, and fertilizer and pesticide runoff from agricultural operations. To keep water from turning into waste, it must be treated (Bhalwe et al., 2022).

One way to treat contaminated water is by coagulation. It involves mixing chemicals or natural materials with water to change the physical characteristics of the suspended and dissolved solids, which facilitates flocculation or sedimentation. (Bhalwe and others, 2022).

The coagulation-flocculation process is a frequently utilized and crucial phase in the treatment of water and wastewater because of its affordability and ease of usage. Coagulation-flocculation is often used as a pre- or post-treatment phase, regardless of the kind of treated sample (such as different kinds of water or wastewater) and the overall treatment plan that is being used. Enhancing the coagulation stage's efficiency seems to be a crucial component in raising the total treatment efficiency as the effectiveness of coagulation-flocculation has a significant impact on the entire treatment performance. Coagulation-flocculation therapy may be broken down into two separate steps that should be used one after the other. The first, known as coagulation, is the process by which a particular colloidal suspension or solution becomes unstable. Coagulation serves the purpose of overcoming the element that supports a system's stability. It is performed with the addition of suitable chemicals, mainly aluminium or iron salts, the so-called coagulant agents. The second sub-process, dubbed flocculation, relates to the induction of destabilized particles in order to come together, to establish contact and so, to form big agglomerates, which may be separated easily generally by gravity settling, (Tzoupanos & Zouboulis, 2014)

The poor treatment and disposal of wastewater pose harm to the environment and human health, making wastewater management a critical challenge on a worldwide scale. Synthetic chemical coagulants are extensively employed in traditional wastewater treatment techniques to remove suspended particles and contaminants. The usage of these substances raises issues however, because of the probable damage they might inflict to ecosystems and human health. Because they may efficiently treat wastewater without posing any environmental risks, natural coagulants derived from plant materials have gained attention as an alternative. The purpose of this study is to assess the environmental benefits and efficacy of treating wastewater using a natural coagulant.

MATERIALS AND METHOD

A. PREPARATION OF MIXED DYE SOLUTION

The mixed dye was purchased from Pyrex laboratory equipment limited company, Benin city, Edo state, Nigeria. 1g of mixed dye was dissolved in 1L of distilled water to create a stock solution of 1g/L, which was then preserved in jars for further use. By diluting the stock solution with distilled water, several working solutions with varying concentrations of mixed dye utilized in this experiment were created. Using a UV Spectrophotometer, separate examination was conducted at the maximum wavelength of 605 nm. One way to get the desired pH in each of the working solutions was to add the appropriate amount of 0.1M sodium hydroxide and 0.1M hydrochloric acid solution

B. PREPARATION OF THE CLAY POWDER

Upon acquisition, the clay was carefully crushed, and the clay were preserved. Subsequently, the clay underwent a meticulous cleansing and drying process to ensure their purity. After this initial preparation, the clay was subjected to a controlled carbonization process at a temperature of 200°C and ground, resulting in their transformation into a fine powder. This powdered form was then subjected to a precise sieving process, utilizing a mesh with a 1.18 mm aperture. During this sieving process, the finer particles were retained for further use.

C. MODIFICATION OF THE CLAY POWDER

The powdered clay was mixed with titanium dioxide of the ratio 7:3 and then the ratio of ethylene glycol with the mixed clay was 1:2. The powder was dried at 600^{o}C in a furnace to remove the moisture present. Then characterization was carried out.

D. ADSORPTION STUDIES

Adsorption studies were carried out in multiple locations to ascertain the effects of the variables influencing the adsorption process to achieve the greatest dye clearance feasible. The investigation encompassed the enhancement of numerous functional elements. The initial concentration (50, 75, 100, 125, 150 mg/l), temperature (30, 40, 50, 60, 70 C), adsorbent dosage (0.5, 1, 1.5, 2,2.5 g), pH (2, 4, 5, 8, 11), and contact time (30, 40, 50, 60, 75 min) were these parameters. During each run, the values of only one parameter were changed at a time; the values of the other parameters remained the same. The ideal value of the preceding parameter is also utilized in the ensuing runs. After the solution is filtered at the conclusion of each run, the filtrate is analysed using a UV spectrophotometer with a maximum wave length of 605nm.

E. DETERMINATION OF THE EFFECT OF ABSORBENT DOSAGE

Investigation of the effect of absorbent dosage was performed by creating a photocatalyst-wastewater mixture of the activated kaolin clay powder and the inactivated kaolin clay powder with various absorbent doses of 0.5g/l, 1.0g/l, 1.5g/l, 2.0g/l and 2.5g/l, and making use of a catalyst pH value which was 2. Values of other parameters such as; temperature, absorbent dosage, dye concentration, $_{P}$H and contact time. Samples were withdrawn and analysed for percentage of colour removal for each of the various absorbent dosage in order to pick the best result, the determination of the best catalyst is a function of the COD value of the mixture.

$$(\%) \text{ removal} = \frac{Ct_{initial} - Co_{final}}{Ct_{initial}}$$

F. DETERMINATION OF THE EFFECT OF PH

Investigation of the effect of pH was carried out by creating and varying the mixture of the wastewater and the optimum performing catalyst into different pH values of 2, 4, 5, 8 and 11. The best catalyst dosage obtained from the determination of the effect of absorbent dosage is used and kept constant throughout the variation of the pH values of other parameters that were kept constant are absorbent dosage: 1,5g/l, contact time: 75mins, dye concentration: 100mg/l, temperature: 30^{o}C. The various samples were withdrawn and analysed for percentage of colour removal.

G. DETERMINATION OF THE EFFECT OF CONTACT TIME

Investigation of the effect of contact time was carried out by varying the mixture of the wastewater sample and the photocatalyst at different values between 30-75mins. The best catalyst and the best pH deduced from previous investigation are used in the determination of contact time. Parameters such as pH, absorbent dosage, dye concentration and temperature were kept constant at 2, 1,5g/l, 100mg/l and 30°C respectively. The various samples were withdrawn and analysed for percentage of colour removal.

H. DETERMINATION OF THE EFFECT OF TEMPERATURE

Investigation of the effect of temperature was carried out by varying the mixture of the wastewater sample and the photocatalyst at different values between 30-70°C. The best catalyst, pH and contact time deduced from previous investigation are used in the determination of temperature. Parameters such as pH, absorbent dosage, dye concentration and contact time were kept constant at 2, 1,5g/l, 100mg/l and 75mins respectively. The various samples were withdrawn and analysed for percentage of colour removal.

I. DETERMINATION OF THE EFFECT OF MIXED DYE CONCENTRATION

Investigation of the effect of mixed dye concentration was carried out by varying the mixture of the wastewater sample and the photocatalyst at different values between 50-150mg/l. The best absorbent dosage, pH, contact time, temperature deduced from previous investigation are used in the determination of mixed dye concentration. Parameters such as pH, absorbent dosage, temperature and contact were kept constant at 2, 1,5g/l, 30°C and 75mins respectively. The various samples were withdrawn and analysed for percentage of colour removal.

ADSORPTION KINETICS

After the adsorption studies and optimum for different parameter was obtained, the kinetics of adsorption were studied using the inactivated and activated clay. Different concentrations of dye were prepared; 50, 75, 100, 125, 150 mg/l. optimum pH of 2, and optimum dosage of 1.5g obtained from adsorption studies was used to carry out the kinetics. The kinetics of adsorption was determined by analysing adsorptive uptake of mixed dye from the solution at different time interval of 30, 40, 50, 60 and 70 min. the data obtained were treated with different kinetic models such as pseudo first order, pseudo second order and intra particle diffusion model.

ADSORPTION ISOTHERM

The isotherm also of adsorption were attained using the inactivated and activated clay. Different concentrations of dye were prepared; 50, 75, 100, 125, 150 mg/l and also an optimum pH of 2, and optimum dosage of 1.5g obtained from adsorption studies was used to carry out the isotherm. The isotherm of adsorption was determined by analysing adsorptive uptake of m from the solution at different time interval of 30, 40, 50, 60 and 75 min. the data obtained were treated with different isothermal models such as the Freundlich model and the Langmuir model.

CHARACTERIZATION OF THE KAOLIN CLAY

The Rolab Research and Diagnostic Laboratory in Ibadan received 20g of each of the activated and inactivated samples, and used a range of analytical instruments to investigate and describe them. These instruments included:

i. Fourier transform infrared (FTIR) spectroscopy
ii. Energy Dispersive x-ray spectroscopy (EDX)
iii. X-ray Diffusion (XRD)
iv. X-ray Fluorescence (XRF)
v. Scanning Electron microscopy (SEM)

RESULTS

A. EFFECT OF ADSORBENT DOSAGE.

The study of the effect of adsorbent dosage on adsorption of mixed dye with inactivated and activated clay gave the result below.

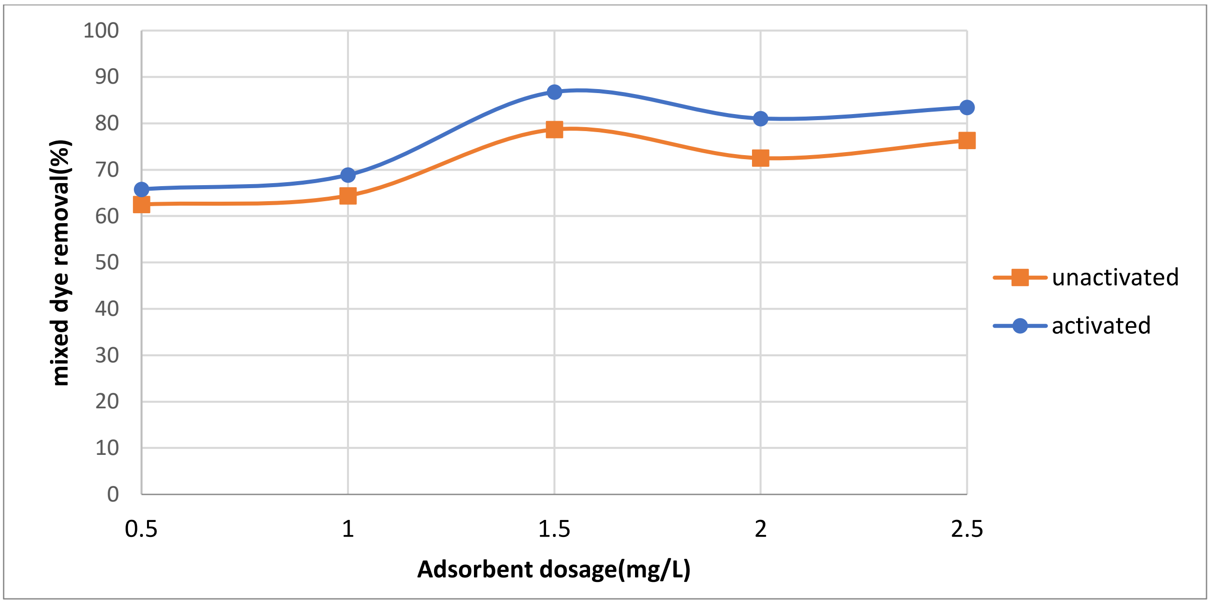


Figure 1: variation of mixed dye (%) with adsorbent dosage

With different amounts of the adsorbent, ranging from 0.5g to 2.5g, with 100ml of 100 mg /L mixed dye solution at 30ºc for 75min, the effect of the adsorbent quantity on mixed dye adsorption was investigated. The figure above displays the experiment's findings in the form of a graph showing the amount of adsorbent dosage against % elimination for both activated and inactivated clay. The outcome demonstrates that as adsorbent dose was raised, the percentage of mixed dye removed increased up to 1.5g and then started to decrease progressively. An optimal dosage of 1.5g of adsorbent—both activated and inactivated was attained. For the inactivated and activated clay, the percentage of mixed dye elimination was 78.67% and 86.75%, respectively.

B. EFFECT OF CONTACT TIME

The study of the effect of contact time on adsorption of mixed dye with inactivated and activated clay gave the result below.

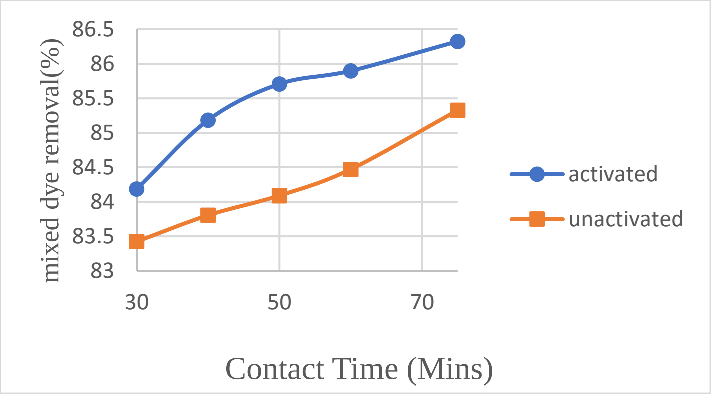


Figure 2: variation of mixed dye (%) with contact time

The effect of contact time on mixed dye adsorption was tested by contacting 1.5g of the adsorbent with 100ml of 100 mg/l mixed dye solution at 30ºc for different time range of 30,40,50,60 and 75min for both activated and inactivated clay. In Figure 4.2, the study's outcome, illustrates how the mixed dye was removed at the beginning of the process, with over 84 % and 83 % mixed dye removed with inactivated and activated clay respectively within 30min and then continued to increase gradually until reaching optimum at 75 min for inactivated and activated clay with an elimination of roughly 85.3% and 86.3% respectively. This kind of behaviour is normal when the adsorbent surface has multiple adsorption sites that progressively become saturated with the dye during longer contact durations.

C. EFFECT OF pH

The study of the effect of pH on adsorption of mixed dye with inactivated and activated clay gave the result below.

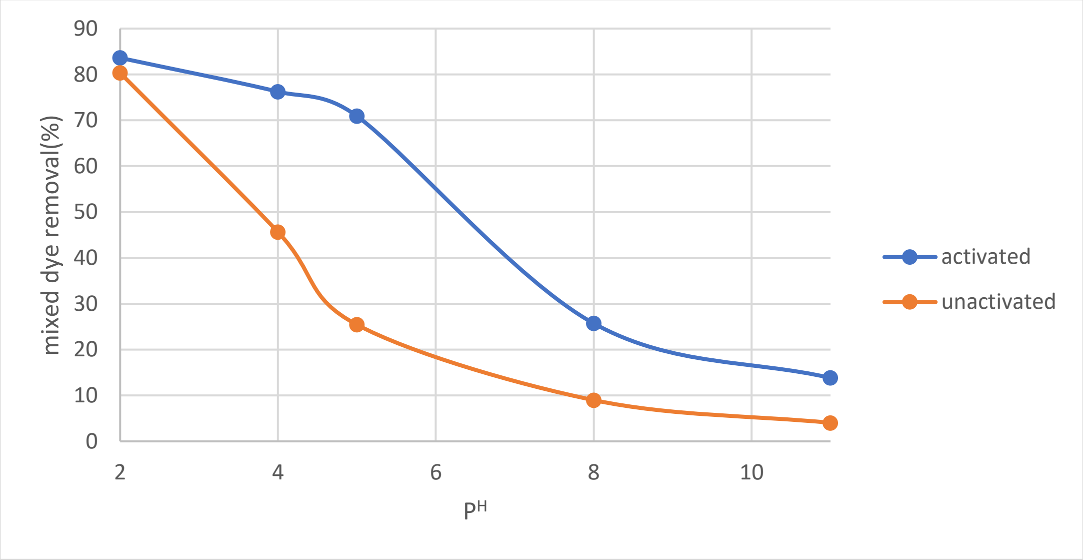


Figure 3: variation of mixed dye (%) with pH

The effect of the pH of the solution on the adsorption of mixed dye was studied by buffering the adsorptive solutions of 100ml of 100mgL^{-1} solution in the pH range of 2,4,5,8 and 11 at 30ºc for a contact time of 75 min. from the studies above we can see that there is a decrease from acidic medium to alkaline medium (2 to 11). The optimum pH is 2 because it had the highest dye removal percentage.

D. EFFECT OF INITIAL DYE CONCENTRATION

The study of the effect of initial dye concentration on adsorption of mixed dye with inactivated and activated clay gave the result below.

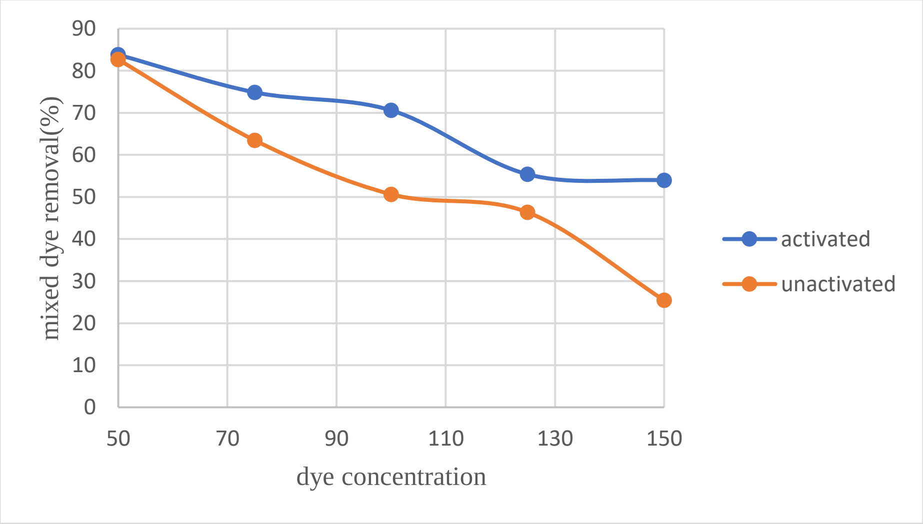


Figure 4: variation of mixed dye (%) with dye concentration

In Figure 4, the experimental results demonstrate that when the starting dye concentration increased from 50 to 150 mg/l, the percentage removal of mixed dyes dropped. This might be because there was less dye accessible for adsorption at a lower dye concentration in comparison to the number of active sites on the adsorbent (clay). In other words, there was a significant difference in the concentration of the adsorbent and dye. Higher concentrations made more mixed dye available, and a high initial concentration of the adsorbent is essential to overcoming the resistance of the dye molecules to bulk or mass transfer from the aqueous phase to the solid-liquid interface. The result shows that the percentage dye removal at 50mg/l are 82% and 83% for inactivated and activated respectively.

E. EFFECT OF TEMPERATURE

The study of the effect of temperature on adsorption of mixed dye with inactivated and activated clay gave the result below.

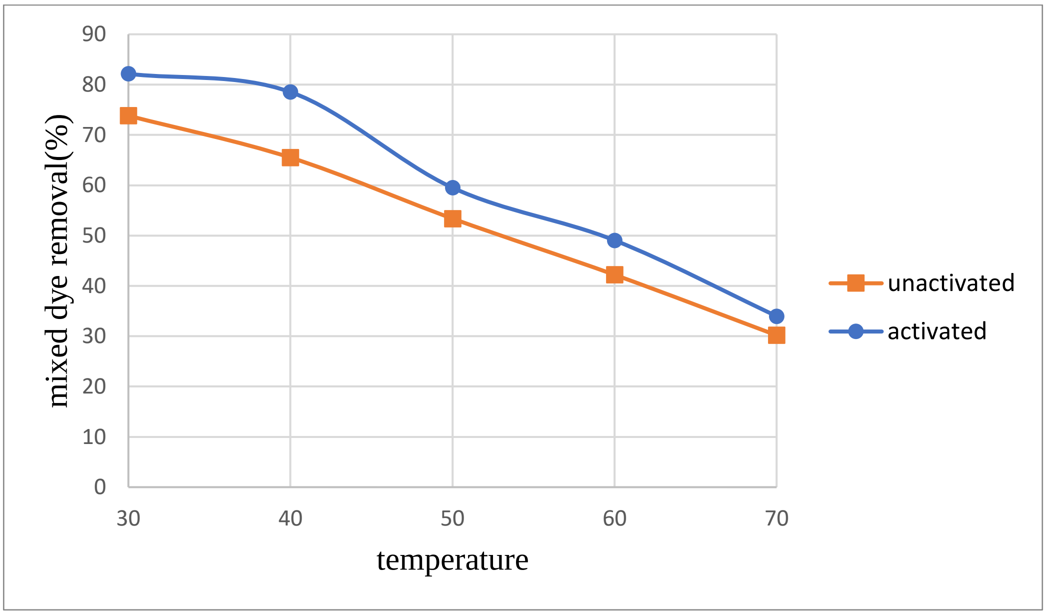


Figure 5: variation of mixed dye (%) with temperature

The effect of the temperature of the solution on the adsorption of mixed was studied by buffering the adsorptive solutions of 100ml of 100mgL^{-1} solution in different temperature range of 30, 40, 50, 60 and 70 at for a contact time of 75 min, The result shows that the percentage dye removal at 30^{o}c are 73% and 82% for inactivated and activated respectively.

F. ADSORPTION KINETIC FOR ACTIVATED

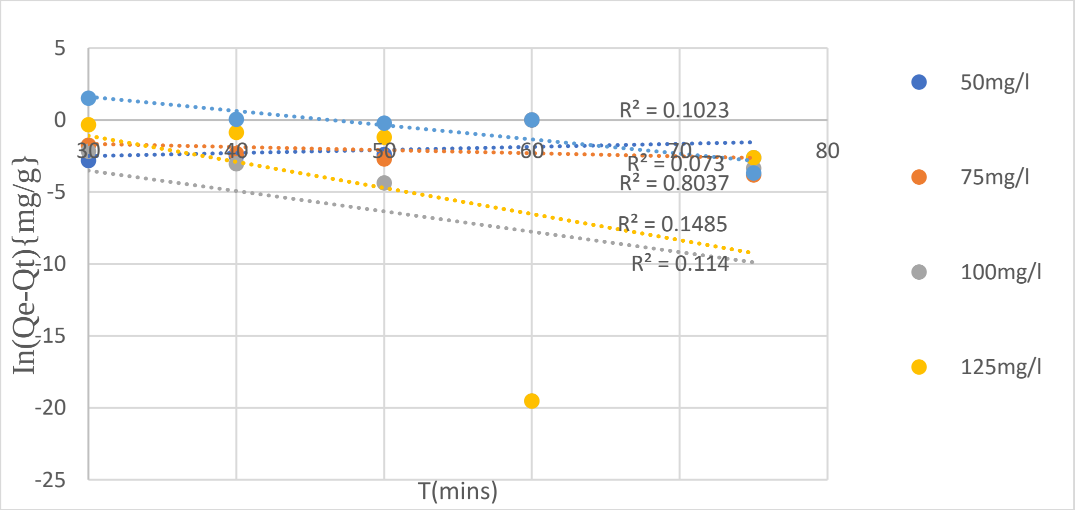


Figure 6: Lager Gren pseudo-first order model plot for adsorption of mixed *dye*

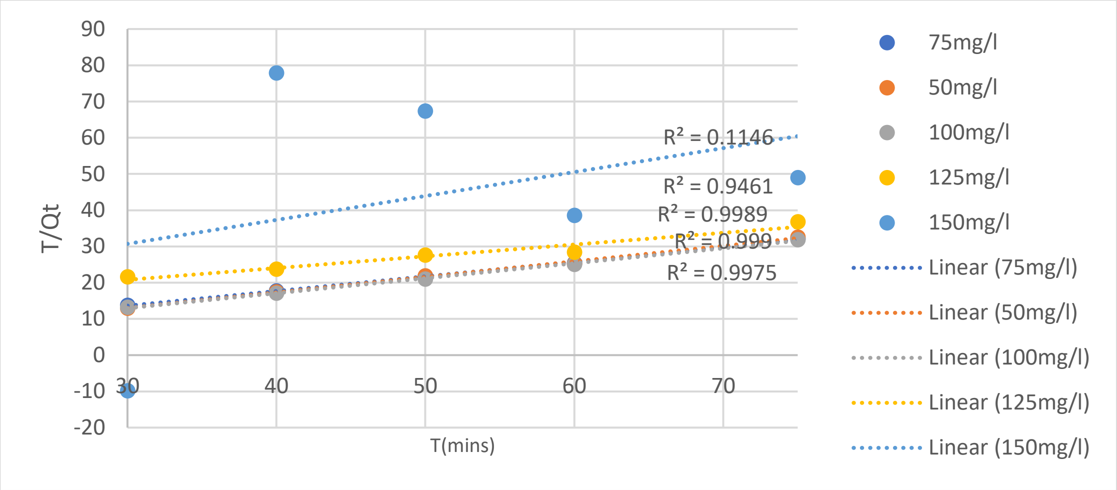


Figure 7: pseudo-second order model plot for adsorption of mixed dye

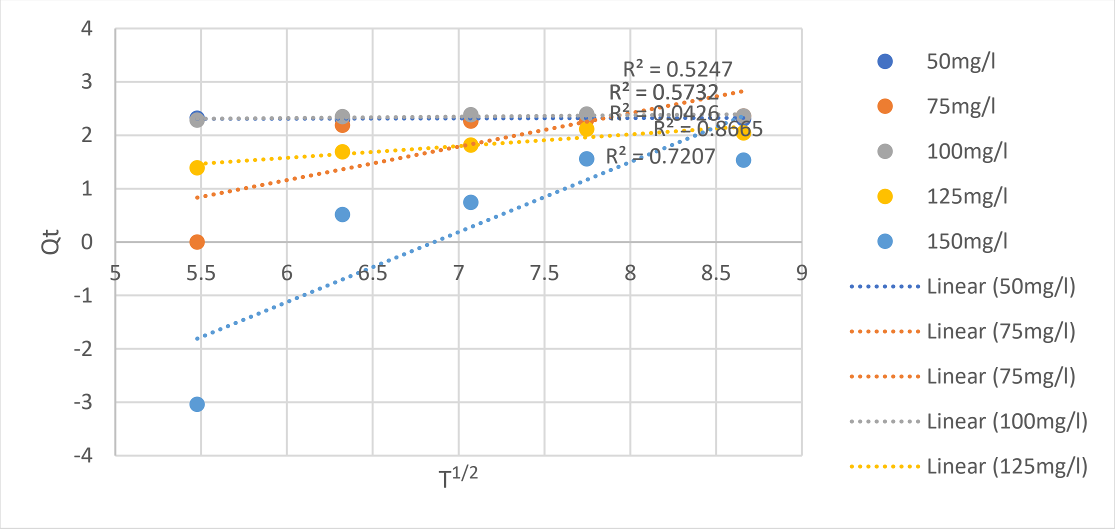


Figure 8: Intra particle diffusion model plot for adsorption of mixed dye

The kinetics of the adsorption process were assessed using contact time of 30, 40, 50, 60 and 75min determine rate constants and equilibrium conditions using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Figure 6, 7 and 8 shows the kinetic constants of the calculated kinetic parameter values and the corresponding correlation coefficient derived from the three kinetic models. The results indicated that pseudo first-order kinetic application was ineffective for dye removal by activated clay. This can be seen by the low value of the R^2 value in figure 6.

The plots of the pseudo-second-order kinetics for mixed dye adsorption onto clay at various concentrations were tested as shown Figure 7. the result shows that correlation coefficients (R^2) for the pseudo-second-order kinetic plots were more than 0.94 which is close to unity. Intra particle diffusion model was also tested. The plot is shown in figure 8. The result indicated shows the R^2 values were low. Hence Only the pseudo-second-order and of the examined kinetic models adequately fit the experimental results for mixed dyes adsorption using snail shell and floor tiles. The high R^2 values for pseudo-second-order kinetic model is an indication of chemisorption process with heterogeneous reaction.

G. ADSORPTION KINETIC FOR UNACTIVATED

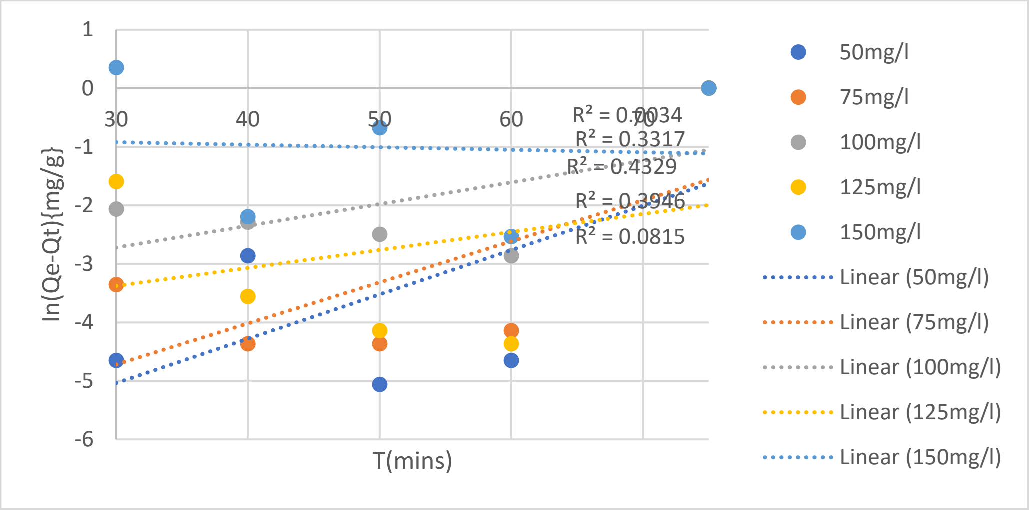


Figure 9: Lager Gren pseudo-first order model plot for adsorption of mixed dye

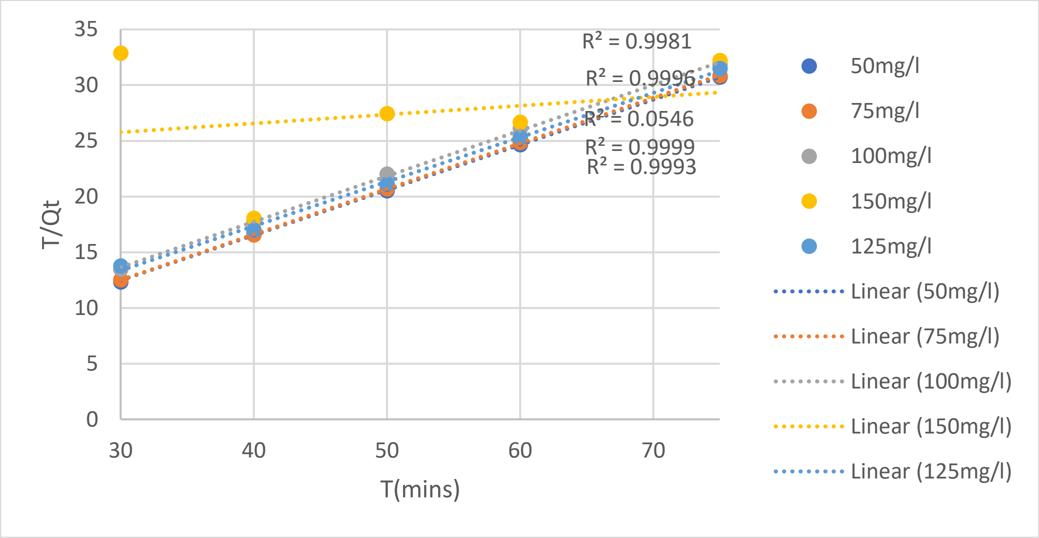


Figure 10: pseudo-second order model plot for adsorption of mixed dye

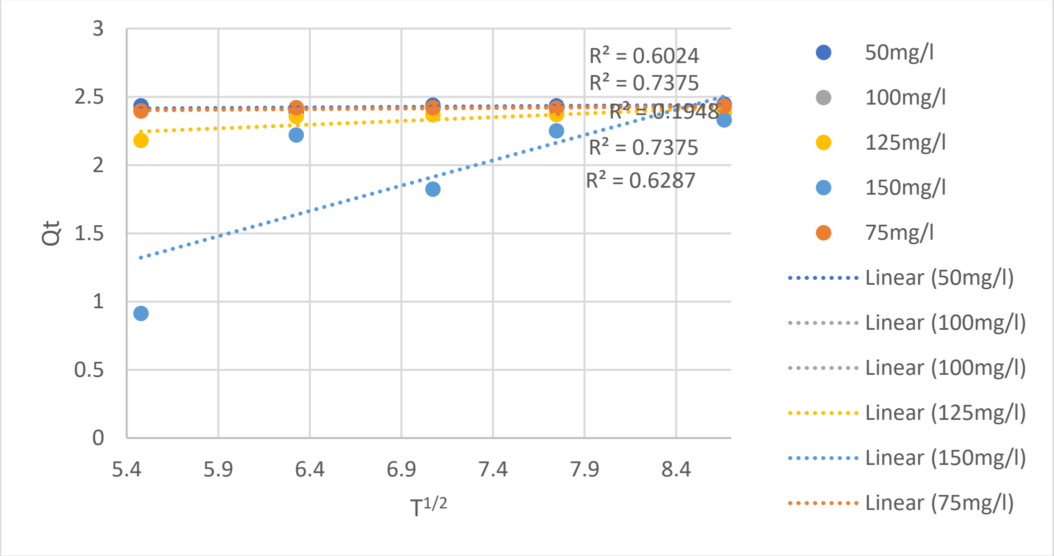


Figure 10: Intra particle diffusion model plot for adsorption of mixed dye

The kinetics of the adsorption process were assessed using contact time of 30, 40, 50, 60 and 75min determine rate constants and equilibrium conditions using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Figure 9, 10 and 11 shows the kinetic constants of the calculated kinetic parameter values and the corresponding correlation coefficient derived from the three kinetic models. The results indicated that pseudo first-order kinetic application was ineffective for dye removal by inactivated clay. This can be seen by the low value of the R^2 value in figure 9.

The plots of the pseudo-second-order kinetics for mixed dye adsorption onto clay at various concentrations were tested as shown Figure 10. the result shows that correlation coefficients (R^2) for the pseudo-second-order kinetic plots were more than 0.91 which is close to unity. Intra particle diffusion model was also tested. The plot is shown in figure 11. The result indicated shows the R^2 values were low. Hence Only the pseudo-second-order and of the examined kinetic models adequately fit the experimental results for mixed dyes adsorption using kaolin clay. The high R^2 values for pseudo-second-order kinetic model is an indication of chemisorption process with heterogeneous reaction.

H. ADSORTPION ISOTHERM FOR ACTIVATED

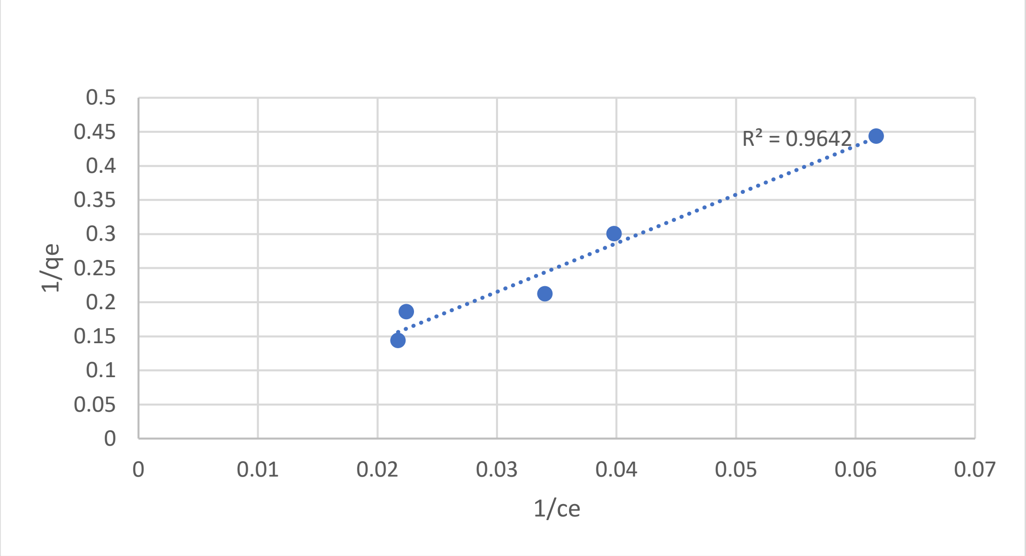


Figure 11: Langmuir model plot for adsorption of mixed dye

Table 4. 1 Langmuir model constant

Initial conc.	Abs	Ce	Qe	1/Ce (Langmuir)	1/Qe (Langmuir)
50	0.072	16.19459	2.253694	0.061749009	0.443715988
75	0.26	25.13136	3.324576	0.039790923	0.300790236
100	0.35	29.4096	4.706027	0.034002503	0.212493484
125	0.67	44.62112	5.358592	0.022410912	0.186616186
150	0.7	46.0472	6.930187	0.021716847	0.144296258

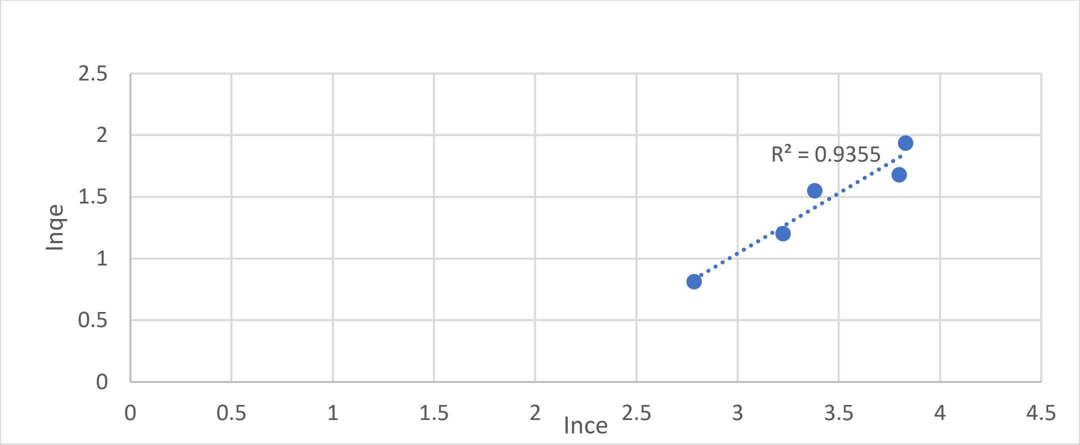


Figure 12: Freundlich model plot for adsorption of mixed dye

Table 4.2: Freundlich model constant

Initial conc.	Abs	Ce	Qe	In (Ce)	In (Qe)
50	0.072	16.19459	2.253694	2.784677	0.812571
75	0.26	25.13136	3.324576	3.224116	1.201342
100	0.35	29.4096	4.706027	3.381321	1.548844
125	0.67	44.62112	5.358592	3.798207	1.678701
150	0.7	46.0472	6.930187	3.829667	1.935887

For the adsorption isotherm model for the activated, the Freundlich isotherm was seen to be the best fit of the models.

I. ADSORTPION ISOTHERM FOR UNACTIVATED

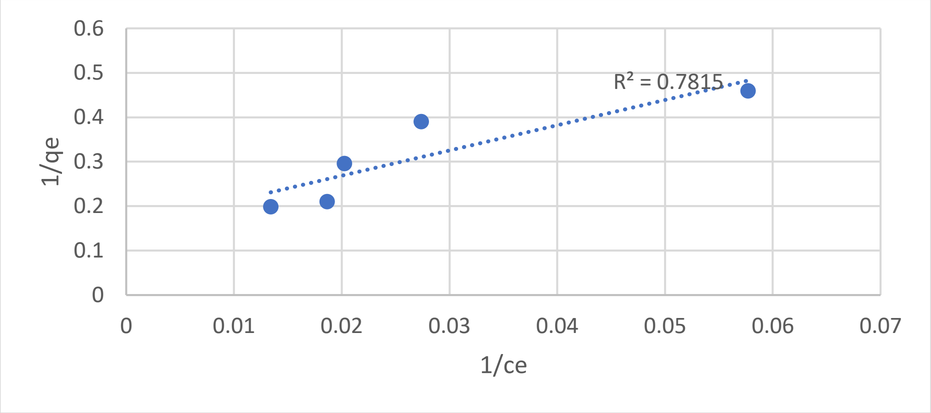


Figure 13: Langmuir model plot for adsorption of mixed dye

Table 4. 3 Langmuir model constant

Initial Conc.	Abs	Ce	Qe	1/Ce (Langmuir)	1/Qe (Langmuir)
50	0.096	17.33546	2.177636	0.057685243	0.459213513
75	0.5	36.54	2.564	0.027367269	0.390015601
100	0.77	49.37472	3.375019	0.020253279	0.296294658
125	0.86	53.65296	4.756469	0.018638301	0.210239976
150	1.3	74.5688	5.028747	0.013410434	0.198856707

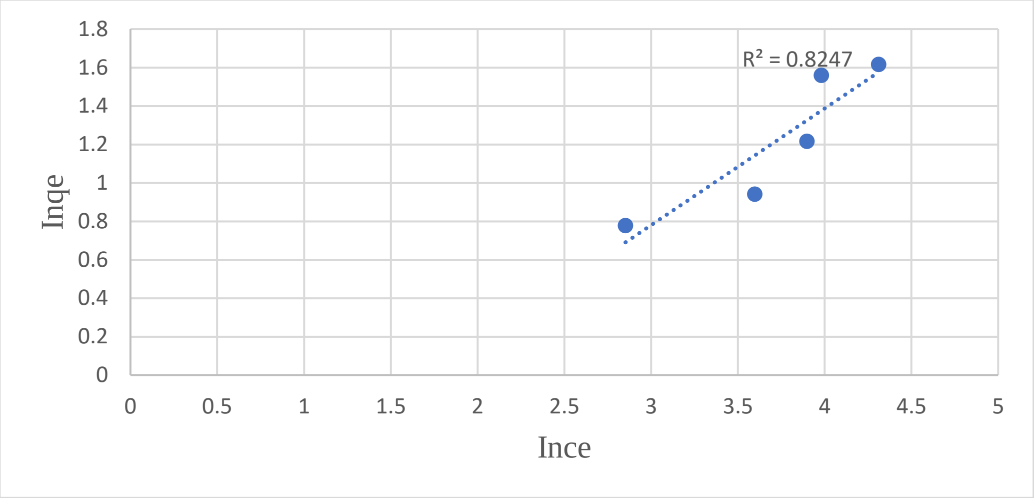


Figure 14: Freundlich model plot for adsorption of mixed dye

Table 4. 4 Freundlich model constant

Initial conc.	Abs	Ce	Qe	In (Ce)	In (Qe)
50	0.096	17.33546	2.177636	2.852754	0.77824
75	0.5	36.54	2.564	3.598408	0.941569
100	0.77	49.37472	3.375019	3.899439	1.216401
125	0.86	53.65296	4.756469	3.982537	1.559506
150	1.3	74.5688	5.028747	4.311722	1.615171

For the adsorption isotherm for inactivated, the Freundlich isotherm best fit the model.

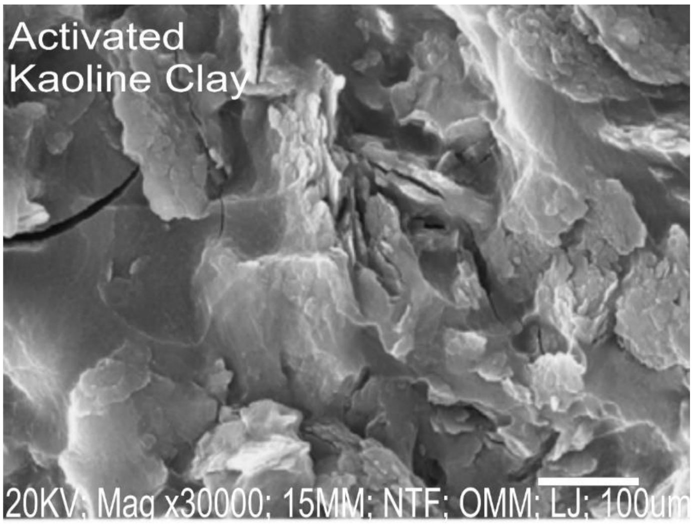


Figure 15: SEM for activated kaolin clay (15MM)

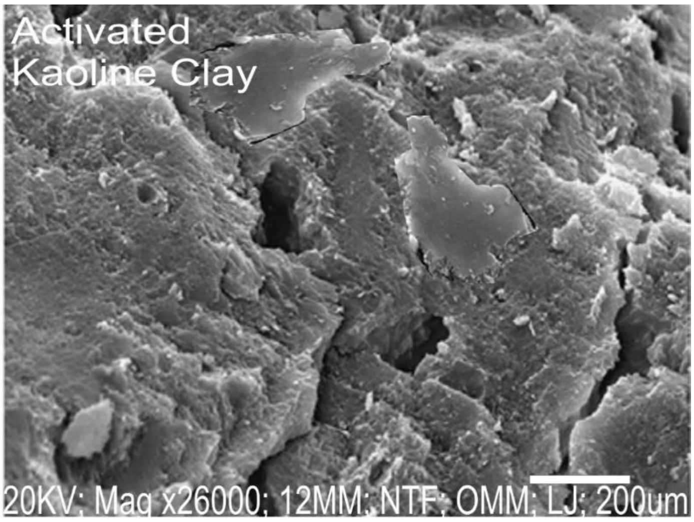


Figure 16: SEM for activated kaolin clay (12MM)

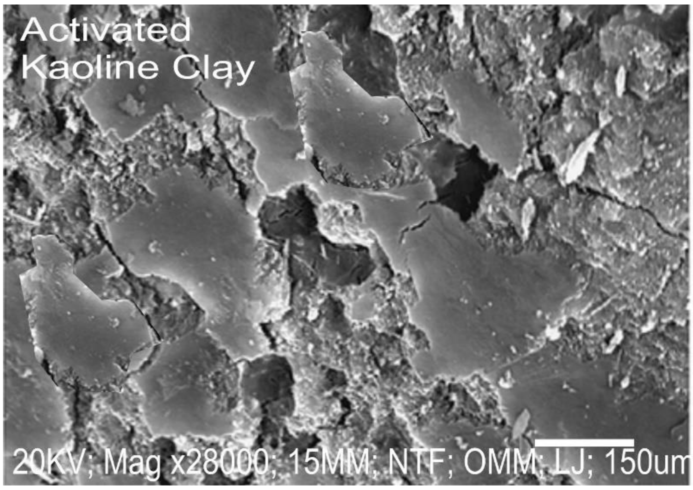


Figure 17: SEM for activated kaolin clay (15MM)

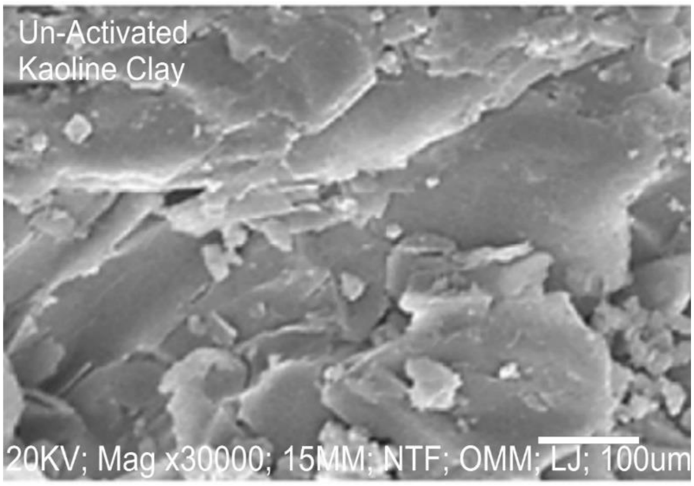


Figure 18: SEM for inactivated kaolin clay(15MM)

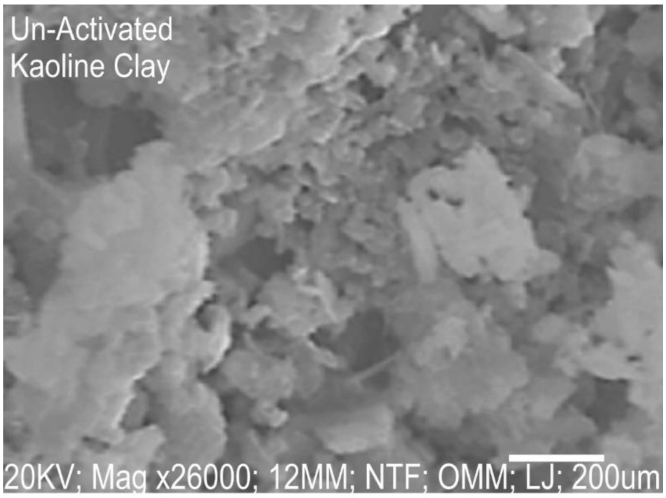


Figure 19: SEM for inactivated kaolin clay(12MM)

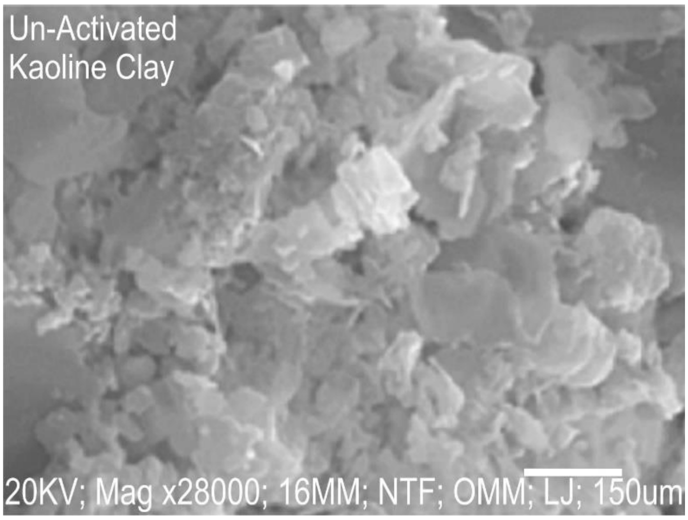


Figure 20: SEM for inactivated kaolin clay

The Scanning Electron Microscopy (SEM) analysis of kaolin reveals significant insights into its microstructural characteristics. SEM images typically show kaolin particles exhibiting a flaky texture with well-defined hexagonal shapes, indicative of its crystalline nature. The morphology of kaolin can vary depending on treatment; for instance, untreated kaolin often displays irregular and agglomerated particle shapes, while acid-treated kaolin may show more dispersed and uniform particle distributions due to the leaching of aluminium ions. This treatment enhances the silicon content while reducing aluminium levels, as observed in the elemental analysis. The high-resolution images obtained from SEM allow for detailed observation of the particle size, shape, and surface texture, which are crucial for understanding the material's physical properties and potential applications. Additionally, the SEM analysis helps identify the bonding structures within the clay and any interactions with additives, providing a comprehensive view of how these factors influence the overall performance of kaolin in various industrial applications. Overall, SEM serves as a vital tool in characterizing kaolin’s microstructure and elucidating the effects of different treatments on its properties.

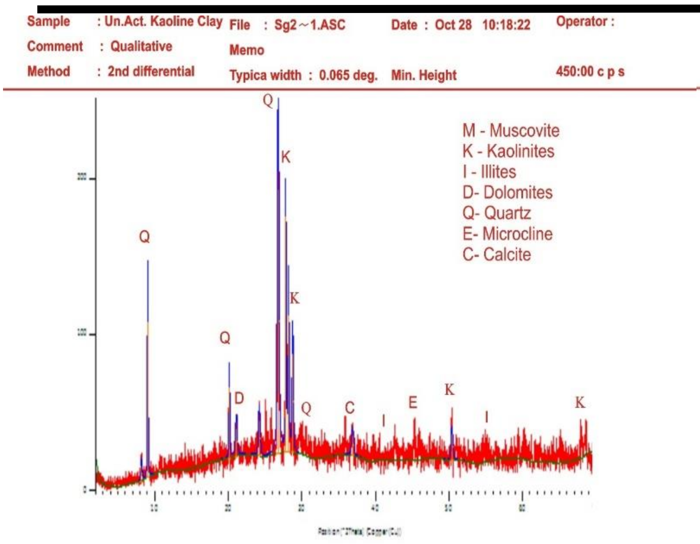

Sample : Un.Act. Kaoline Clay
Comment : Qualitative
Method : 2nd differential
File : Sg2~1.ASC
Memo
Typica width : 0.065 deg.
Date : Oct 28 10:18:22
Min. Height
Operator :
450:00 c p s

Figure 21: XRD for inactivated kaolin clay

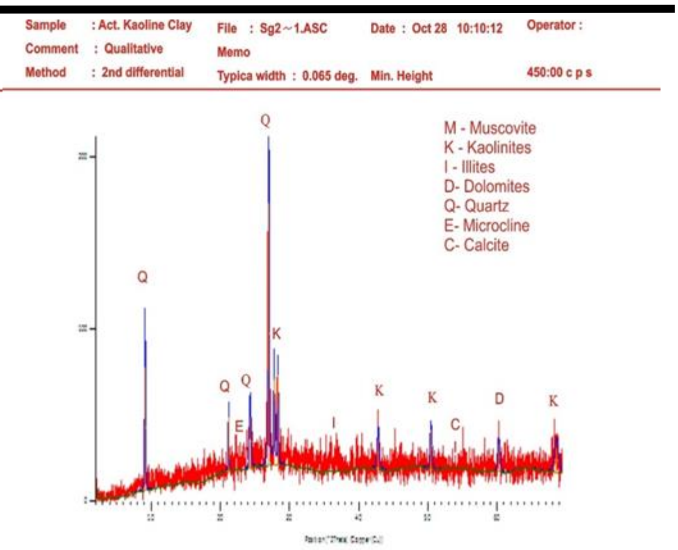
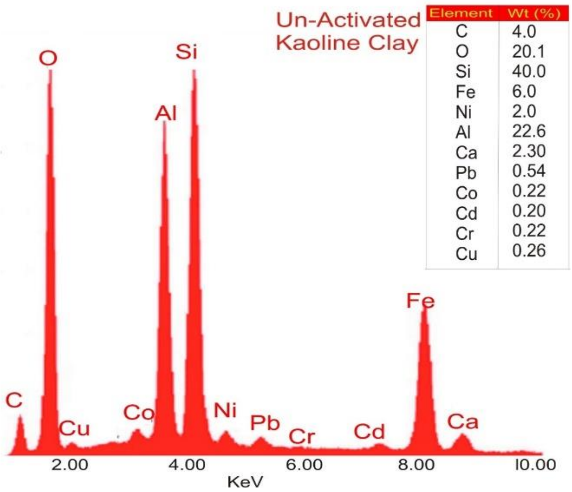

Sample : Act. Kaoline Clay
Comment : Qualitative
Method : 2nd differential
File : Sg2~1.ASC
Memo
Typica width : 0.065 deg.
Date : Oct 28 10:10:12
Min. Height
Operator :
450:00 c p s

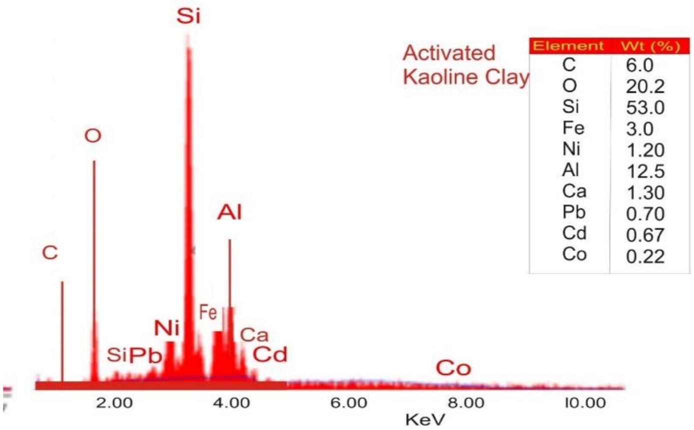
Figure 22: XRD for Activated kaolin clay

The X-ray diffraction (XRD) patterns for un-activated and activated kaolin clay samples reveal significant differences in their crystalline structures. Both samples contain similar mineral components, including quartz (Q), kaolinite (K), muscovite (M), illite (I), dolomite (D), microcline (E), and calcite (C). However, the activated sample shows notably higher peak intensities, particularly for quartz, suggesting an increase in crystallinity or better-defined crystal structures after activation. The quartz peaks are dominant in both samples, but they appear more pronounced in the activated clay. Conversely, the kaolinite peaks seem relatively stronger in the un-activated sample, indicating that the activation process may have altered the kaolinite structure or content. The activated sample also exhibits a cleaner diffraction pattern with less background noise, pointing to a more ordered overall structure. These changes in peak intensities, background noise, and subtle shifts in peak positions between the two samples indicate that the activation process has significantly reorganized the clay's structure at the molecular level, potentially enhancing certain properties that could be beneficial for various applications.



Element	Wt (%)
C	4.0
O	20.1
Si	40.0
Fe	6.0
Ni	2.0
Al	22.6
Ca	2.30
Pb	0.54
Co	0.22
Cd	0.20
Cr	0.22
Cu	0.26

Figure 23: EDS for inactivated kaolin clay



Element	Wt (%)
C	6.0
O	20.2
Si	53.0
Fe	3.0
Ni	1.20
Al	12.5
Ca	1.30
Pb	0.70
Cd	0.67
Co	0.22

Figure 24: EDS for Activated kaolin clay

The images present Energy Dispersive X-ray Spectroscopy (EDS) data for un-activated and activated kaolin clay samples. Both samples contain similar elements, but with notable differences in their concentrations. In the un-activated kaolin clay, silicon (Si) is the most abundant element at 40.0%, followed by aluminium (Al) at 22.6% and oxygen (O) at 20.1%. After activation, the silicon content increases significantly to 53.0%, while aluminium decreases to 12.5%, and oxygen remains relatively stable at 20.2%. The activation process also affects other elements: iron (Fe) decreases from 6.0% to 3.0%, carbon (C) increases from 4.0% to 6.0%, and nickel (Ni) slightly decreases from 2.0% to 1.20%. Some trace elements like lead (Pb) and cadmium (Cd) show slight increases after activation. The EDS spectra visually represent these changes, with the activated sample showing a notably higher silicon peak and reduced aluminium peak compared to the un-activated sample. These compositional changes suggest that the activation process alters the clay's structure, potentially enhancing certain properties that could be beneficial for various applications.

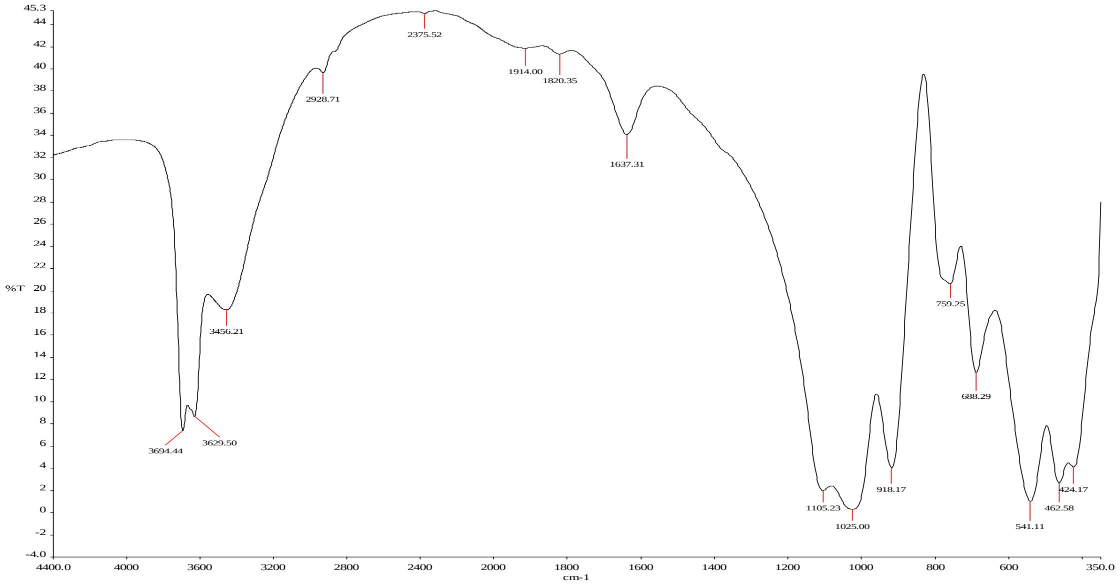


Figure 25: FTIR Inactivated Kaolin + Clay

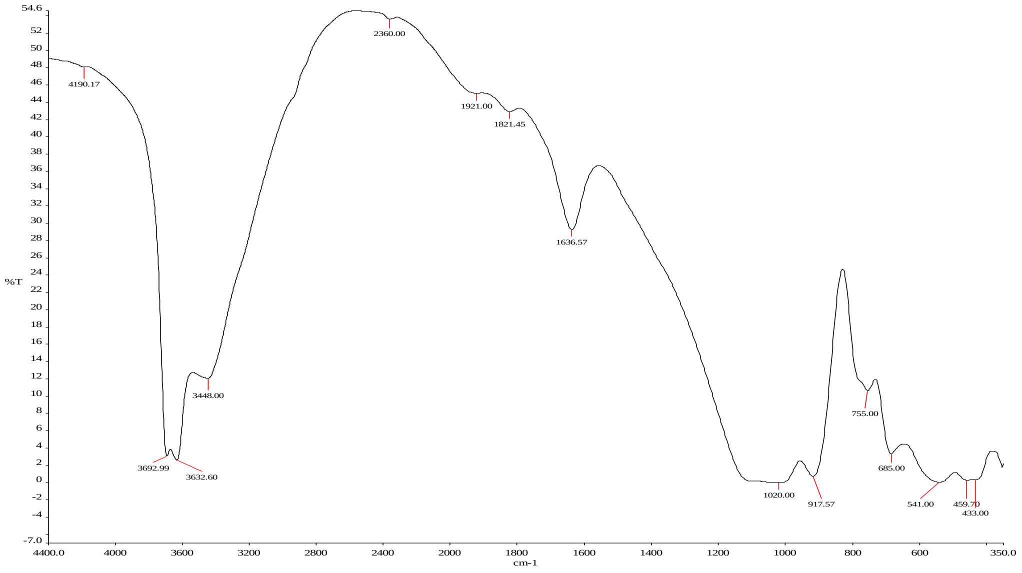


Figure 26: FTIR Activated Kaolin + Clay

Based on FTIR analysis for kaolin, we would expect to see distinct spectral features for both activated and un-activated kaolin mixed with clay. In a typical FTIR spectrum, kaolin (kaolinite) exhibits characteristic peaks that can be affected by the activation process. The hydroxyl (OH) stretching region, usually observed around 3700-3600 cm^-1, would likely show changes in peak intensity or position due to activation. The Si-O stretching band, typically found near 1030 cm^-1, and the Al-OH bending vibration around 915 cm^-1 are also key features that might be altered by activation. For the activated kaolin sample, we might observe increased peak intensities, shifts in peak positions, or the appearance of new peaks, indicating structural changes or the presence of new functional groups resulting from the activation process. The comparison between activated and un-activated kaolin mixed with clay would reveal how the activation process affects the clay's structure and bonding, potentially enhancing its properties for various applications. However, without actual spectral data from the specific samples mentioned in the search results, a more detailed analysis of the FTIR results for these kaolin mixtures is not possible.

CONCLUSION

This study successfully demonstrated the effectiveness of both activated and inactivated kaolin clay, enhanced with titanium dioxide, for the removal of mixed azo dyes from aqueous solutions. The research highlighted that activated kaolin clay exhibited superior adsorption performance due to its increased surface area and porosity, achieving higher dye removal percentages under optimized conditions. Key factors such as adsorbent dosage, contact time, pH, temperature, and initial dye concentration significantly influenced the adsorption process, with optimal conditions identified as 1.5g adsorbent dosage, 75 minutes contact time, pH 2, and 30°C. The pseudo-second-order kinetic model best described the adsorption process, indicating chemisorption as the primary mechanism, while the Freundlich isotherm model confirmed heterogeneous surface adsorption. These findings underscore the potential of kaolin clay as a cost-effective and sustainable alternative for treating dye-contaminated wastewater. The characterization of the adsorbent using techniques like SEM, XRD, EDX, and FTIR provided valuable insights into the structural and chemical properties of the clay, further validating its suitability for dye removal. The study also revealed that the adsorption process was spontaneous and exothermic, with higher efficiency at lower temperatures. Despite the promising results, the research acknowledged limitations such as the need for further optimization and scalability for industrial applications. Future studies could explore the regeneration and reusability of the adsorbent, as well as its performance in real industrial effluents with complex matrices.

In conclusion, this project contributes to the growing body of research on eco-friendly wastewater treatment methods, offering a practical solution to mitigate the environmental impact of synthetic dyes. By leveraging locally available materials like kaolin clay, the study aligns with global efforts to promote sustainable and affordable water treatment technologies. The findings not only advance scientific understanding of adsorption mechanisms but also provide a foundation for future innovations in environmental remediation.

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