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ADSORPTION PERFORMANCE OF SILICA XEROGEL FROM RICE HUSK FOR SIMULTANEOUS REMOVAL OF METHYLENE BLUE AND TARTRAZINE DYES FROM SIMULATED WASTEWATER

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ABSTRACT

This research work assessed the adsorption performance of silica xerogel for removal of binary solution of methylene blue and tartrazine dyes from simulated wastewater. Silica xerogel was extracted from rice husk using sol gel method and modified with 1.0 M HNO_3 (nitric acid). Using batch adsorption methods, the effect of initial concentration, temperature, ionic strength, contact time and adsorbent dosage on adsorption process of methylene blue and tartrazine in wastewater were studied using binary solutions of the dyes. Percentage removal of the dyes studied increased as the initial concentration was varied from 20 ppm to 60 ppm. The removal efficiency decreased as the temperature was varied from 30 to 50℃. The adsorption efficiency showed an increase at higher pH for methylene blue and at lower pH for tartrazine due to their ionic nature. The variation of contact time between 2 and 6 hours showed a sharp increase in dyes removal from 2 to 5 hours but a slow increase after 5 hours. The percentage removal of dyes increased as the adsorbent dosage increased between 0.5 to 2.5 g. The effect of ionic strength on adsorption efficiency decreased as the concentration of NaCl was varied from 0.02 to 0.10 M. The experimental data was tested using adsorption isotherm models of Langmuir, Freundlich and Temkin. Langmuir model was the best fit among the three isotherms used for the analysis as the R^2 and R_L values favoured the isotherm. The data showed that the adsorption process is best described by the pseudo second order kinetics model as the R^2 values for all the dyes were more than those of the pseudo first order model. Therefore, silica xerogel is a potential adsorbent for the uptake of the pollutants in wastewater.

Keywords: Adsorption, methylene blue, rice husk, silica xerogel, tartrazine, wastewater

INTRODUCTION

Environmental pollution is inevitable due to industrialization, urbanization, increasing human population and sophistication in human activities. Enlightenment about the associated

problems has led to a rise in the level of awareness on the significance of reducing the harmful substances contained in the wastewater from manufacturing and processing industries before discharging into the environment [1]. Dyes are very important pollutants in wastewater as colour is the most obvious indicator of water contamination, the presence of small amount in aquatic medium makes it unpleasant [2]. Effluents from some industries are highly coloured and their discharge into rivers and lakes makes water from these sources unfit for domestic, agricultural and industrial purposes [3]. Apart from the adverse effect on the aesthetics of the aquatic environment, dyes make water undesirable for drinking and other recreational purposes because of its abnormal and undesirable appearance. The presence of dyes also has inhibiting effect on the process of photosynthesis, thereby affecting aquatic ecosystem due to reduced light penetration [4].

A number of technologies have been applied over the years for the treatment of dye-containing wastewater. Adsorption method using activated carbon has been widely used because of its simplicity and high efficiency resulting from its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [5]. However, its widespread use is restricted due to relatively high cost and problems like high temperature combustion pore blocking and hygroscopicity associated with its production**.** This has led to the search for new, efficient and cheaper adsorbents for treating dye-bearing wastewater. Numerous alternatives especially agricultural by-products like rice husk, guava leaf powder, wheat shell are being investigated to determine their capacities for removing dyes from wastewater, using methylene blue and tartrazine as the model dyes [6].

Minimal researches have been carried out in terms of removal of binary dyes especially using silica xerogel from rice. Therefore, this study seeks to achieve the novelty in carrying out removal of binary dyes in wastewater since industries discharge wastewater with different types of dyes. The following objectives are to be carried out: (1) to produce silica xerogel from rice husk using sol gel method, the silica xerogel will be modified using nitric acid, (2) simultaneous removal of methylene blue and tartrazine will be carried out under the effect of contact time, concentration, temperature, ionic strength and adsorbent dosage (3). The effects of competitive adsorption on the kinetics and thermodynamics of the adsorption will also be investigated. This research work was carried out in the Research Laboratory, Chemistry Department, Joseph Sarwuan Tarkaa University, Makurdi, between August, 2023 and October, 2023.

EXPERIMENTAL

Sample collection and pretreatment

About 319 g of rice husk was obtained from rice millers in Wurukum, New Bridge Lafia Road, Makurdi, Makurdi Local Governemnt Area of Benue State, Nigeria. The rice husk was sieved and washed with distilled water to remove dust and then dried at room temperature for 48 h [7].

Extraction of silica xerogel from rice husk

The 319 g rice husk obtained above was ashed using a muffle furnace at 600 ^{o}C for 3 h and cooled to room temperature. The rice husk ash was then treated with 200 mL of 1.0 M NaOH and heated at 80 ^{o}C in 250 mL Erlenmeyer flasks for 1 h with constant stirring. The solution was allowed to cool at room temperature and filtered through whatman filter paper (110 mm). The residue was washed with 100 mL of distilled water. The filtrate was treated with 1.0 M HCl with constant stirring. Silica gel precipitated when the pH was less than 10. The silica gel formed was aged for 24 h. The gel was transferred into a beaker and dried at 80 ^{o}C for 12 h to produce xerogel. The silica xerogel sample obtained was subjected to washing with distilled water. All the samples were stored in airtight plastic bottles for further analysis [8]. The equations of the reactions are as follows:

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + 2HCl \longrightarrow SiO_2 + 2NaCl + H_2O \quad (2)$$

Modification of silica xerogel with acid

About 50 g of the extracted silica xerogel was treated with nitric acid. In the modification process, 50 g of silica xerogel wasin equilibrium with 100 mL of the acid in a 500 mL beaker and stirred with a glass rod for 30 minutes and heated at 80 ^{o}C for 1 h. It was cooled and washed with distilled water until the pH of the filtrate turns to neutral and then dried [9].

Preparation of stock solution of adsorbate (Simulated wastewater)

The stock solutions of adsorbate (methylene blue and tartrazine dyes) were obtained by dissolving 1 g of methylene blue and tartrazine in distilled water in a 1000 mL standard flask and made up to mark. The solution was diluted to desired working concentrations with distilled water and stored at room temperature [10].

Adsorption studies

Batch adsorption experiments were carried out to study the equilibrium capacity of the modified silica xerogel in the removal of dyes from simulated wastewater and the effect of initial concentration, ionic strength, contact time, mass of the adsorbent and temperature on the adsorption of methylene blue and tartrazine. About 1.5 g each of the silica xerogel adsorbent was mixed with 50mL of the dye solutions in a100mL flask and the mixture was shaken thoroughly for about 2 h using an electric shaker and was allowed to equilibrate at 28 ^{o}C for 4 h in a thermostatic water bath. Thereafter, the suspension was filtered using whatman (No 1) filter paper and the filtrate was analysed using UV-Vis spectrophotometer (Jenway 7415 Single beam, United States of America). The amount of dyes adsorbed per unit mass was calculated as

$$\text{Adsorption (\%)} = \frac{C_{i-}\, c_f}{c_i} \times 100 \qquad (3)$$

where C_i and C_f are the initial and final metal ion concentrations respectively,

The equilibrium capacity of adsorption is calculated using the formula:

$$q_e = (\, C_o - C_e) \times \frac{V}{M} \qquad (4)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_o (mg/L) and C_e (mg/L) is the initial and equilibrium metal concentration, respectively, V is the volume (L) and(M) isthe amount of the adsorbent [11].

Simultaneous determination of concentration in binary dye mixture

The percentage adsorption of the dyes was determined in binary dye mixture as shown below:

Concentrations of individual dyes (MB and TZ) were obtained using the simultaneous equation method as shown below.

Methylene blue + Tartrazine

$$C_{MB} = \frac{(A_2 a_{TZ1} - A_1 a_{TZ2})}{(a_{MB2} a_{TZ1} - a_{MB1} a_{TZ2})} \qquad (5)$$

$$C_{TZ} = \frac{(A_1 a_{MB2} - A_2 a_{MB1})}{(a_{MB2} a_{TZ1} - a_{MB1} a_{TZ2})} \qquad (6)$$

where A_1 is absorbance of the Methylene blue at λ_1 (662 nm), A_2 is absorbance of the

tartrazine at λ_2 (424 nm), a_{MB1} is molar absorptivity of methylene blue at λ_1 (662 nm), a_{MB2} is molar absorptivity of methylene blue at λ_2 (424 nm), a_{TZ1} is molar absorptivity of tartrazine at λ_1 (424 nm) and a_{TZ2} is molar absorptivity of tartrazine at λ_2 (662 nm).

Effect of initial concentrations

In order to study the effect of initial concentration on the adsorption uptake, 50 mL of adsorbate solutions with known initial concentrations (20, 30, 40, 50 and 60 ppm) were prepared in a series of 50 mL Erlenmeyer flasks. About 1.5 g of adsorbent was placed inside the flask. The flasks were then placed in a shaker at constant temperature of 30 °C, with agitation speed of 150 rpm [12].

Effect of temperature

The adsorption of the dyes on the silica xerogel adsorbent was studied at various temperatures (30, 35, 40, 45 and 50 ^{o}C) with the use of a thermostatic water bath. Exactly 50 mL of dyes solutions was measured into 2 labeled flasks each containing 1.5 g of the adsorbent. The mixtures were shaken for 2 h using an electric shaker at 35 ^{o}C for 4 h. The experimental setup was repeated for 40, 45and 50^{o}C. At the end of each contact time, the content of each flask was filtered and the residual concentration of the pollutants in the filtrates was determined using Ultraviolet visible spectrophotometer (UV) and the amount of dye adsorbed was calculated as described by Ikyereve1 *et al* [13].

Effect of contact time

About 1.5 g of the adsorbent was added to 50mL of simulated wastewater in a 200 mL flask and was shaken for a period of 2, 3, 4, 5, 6 h at constant temperature of 30 ^{o}C using a thermostatic water bath. The solution was filtered, and the filtrate was analyzed for the presence of dyes using Ultraviolet visible spectrophotometer and the amount of dyes removal and adsorption capacity was calculated in each case as earlier stated [11].

Effect of mass of the adsorbent

The adsorption capacity of the modified adsorbent was studied at different adsorbent dosage of 0.5, 1.0, 1.5, 2.0 and 2.5 g. About 50 mL of the dye solutions was mixed with various masses of the modified adsorbent in a 250 mL flask and was shaken for 4 h at 30 ^{o}C. The solution was filtered, and the filtrate analyzed using Ultraviolet visible spectrophotometer [11].

Effect of ionic strength

The adsorption efficiency under ionic strength was determined by varying the concentration of NaCl (0.02, 0.04, 0.06, 0.08, 0.10 M) while dyes solution and adsorbent dosage were kept constant. About 1.5 g of the silica xerogel adsorbent was mixed with 50 mL of the dyes solution in a100 mL flask and 0.02 M of NaCl, the mixture was shaken thoroughly for about 2 h using an electric shaker. Thereafter, the solution was filtered using whatman (No 1) filter paper and the filtrate was analysed using UV-Vis spectrophotometer [14].

RESULTS AND DISCUSSION

Batch adsorption studies

The effect of parametric factors, namely, concentration, contact time, pH, ionic strength, dosage and temperature for the adsorption of dyes in simulated wastewateronto silica xerogel adsorbent were studied. Figures 1 to 6 show the percentage removal of dyes under the factors mentioned in that order.

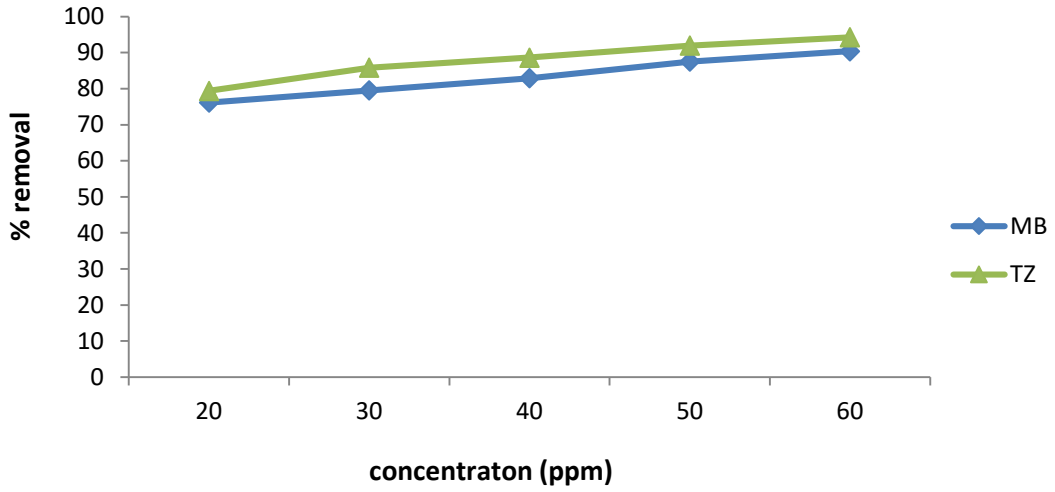

Figure 1: Effect of concentrations on removal efficiency of binary solution of methylene blue and tartrazine onto silical xerogel

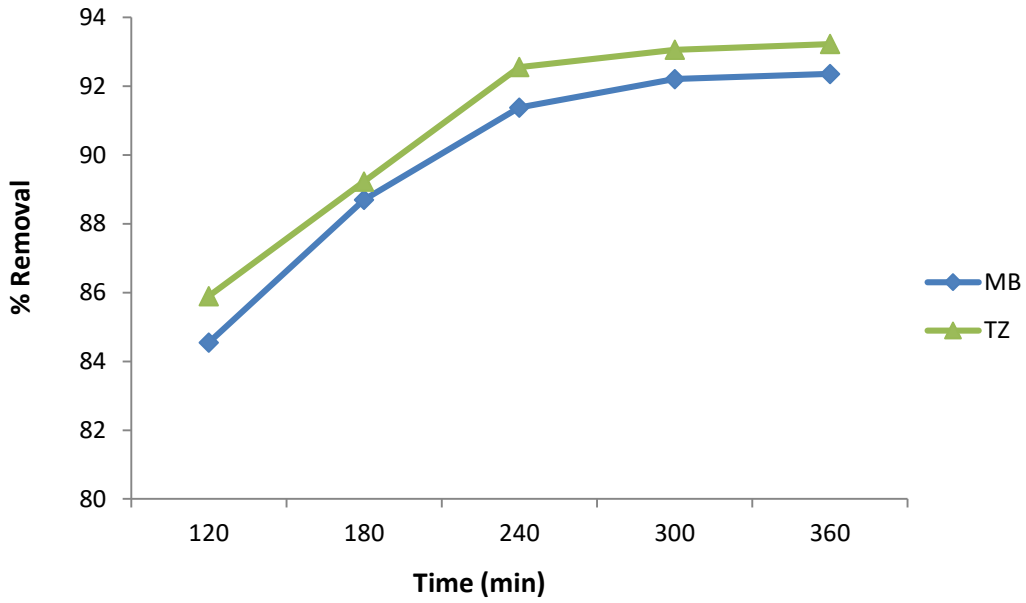

Figure 2: Effect of contact time on removal efficiency of binary solution of methylene blue and tartrazine onto silical xerogel

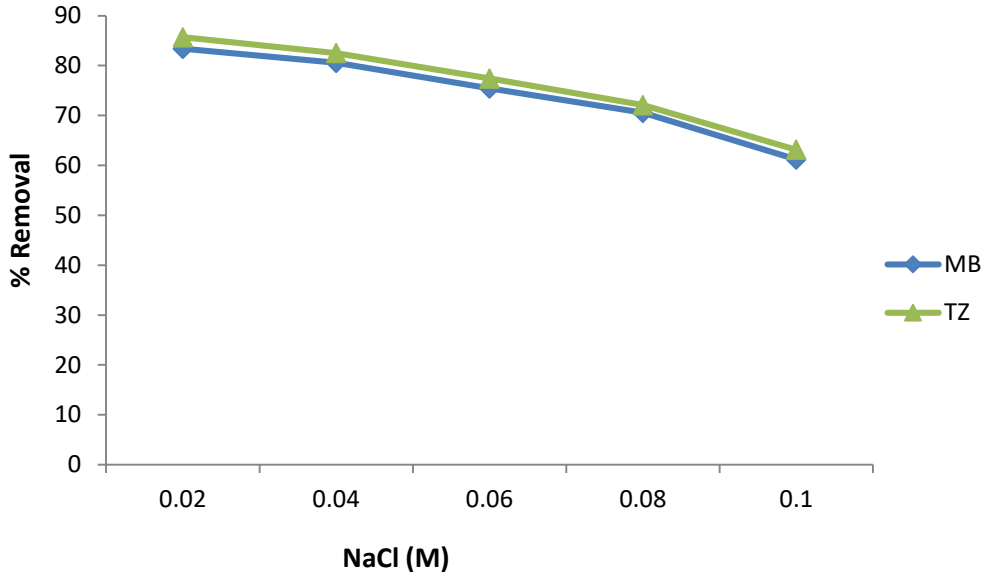

Figure 3: Effect of ionic strength on removal efficiency of methylene blue and tartrazine in wastewater solution onto silical xerogel

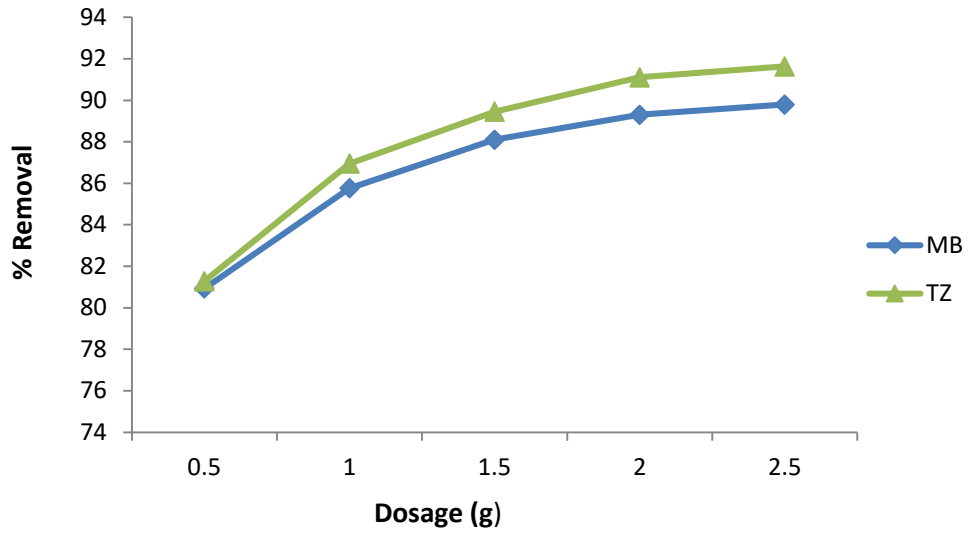

Figure 4: Effect of adsorbent dosage on removal efficiency of methylene blue and tartrazine in wastewater solution onto silical xerogel

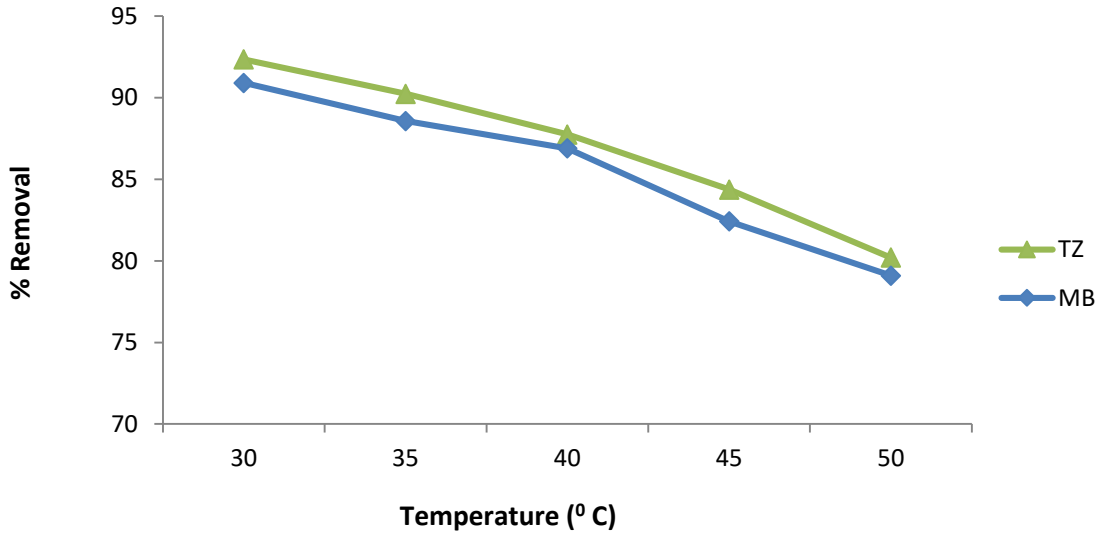

Figure 5: Effect of temperature on removal efficiency of methylene blue and tartrazine in wastewater solution onto silical xerogel

Kinetic models

Kinetic parameters are necessary to determine the best operational conditions in a continuous process of dye removal. To investigate the mechanism of sorption, pseudo first order and second order were used as plotted in Figures 6 and 7. The experimental constants for the kinetic models are presented in Tables 1 and 2.

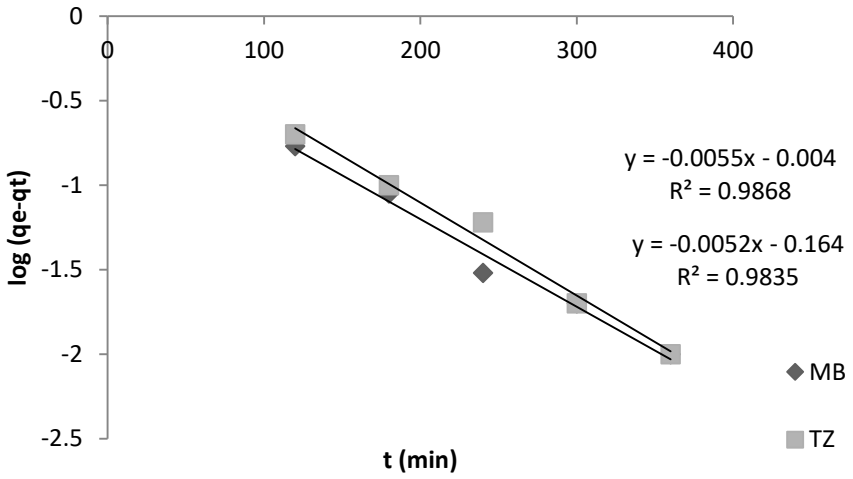

Figure 6: A plot of pseudo first order kinetic for adsorption of methylene blue and tartrazine in wastewater solution onto silical xerogel

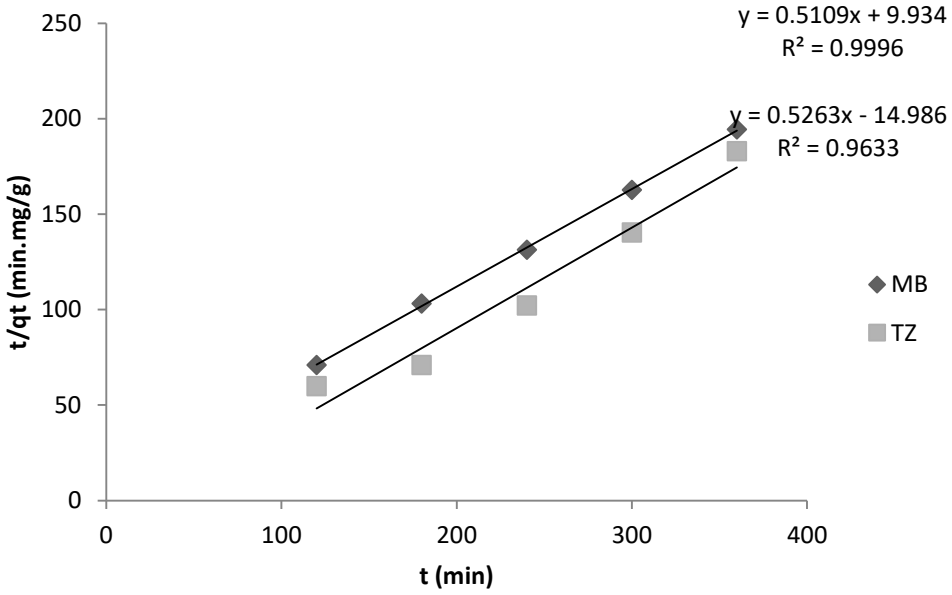

Figure 7: A plot of pseudo second order kinetic for adsorption of methylene blue and tartrazine in wastewater solution onto silical xerogel

Table 1: Pseudo first order kinetics parameters for dye adsorption

DYE	Qexp	Qcal	K_1	%SSE	R^2
MB	1.85	1.01	0.012	0.141	0.986
TZ	1.87	1.45	0.012	0.035	0.983

Table 2: Pseudo second order kinetics parameters for dye adsorption

DYE	Qexp	Qcal	K_2	%SSE	R^2
MB	1.85	1.96	0.026	0.002	0.999
TZ	1.87	1.89	0.019	0.018	0.963

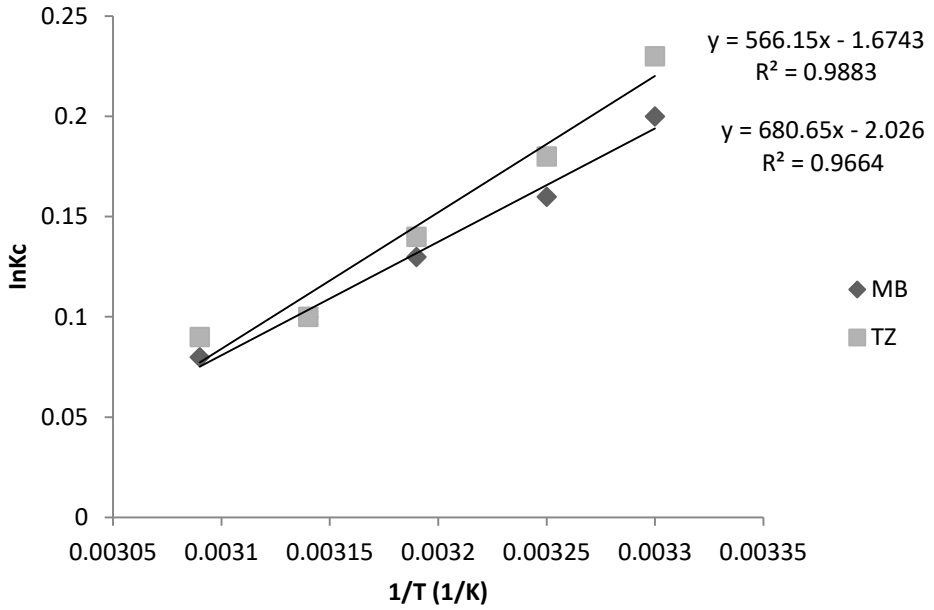

Figure 8: A plot of Van't Hoff thermodynamics model for methylene blue and tartrazine in wastewater solution

Table 3: Van't Hoff thermodynamics parameters

DYE	ΔG (KJ/mol)	ΔH (J/mol)	ΔS (J/mol k)	R^2
MB	-489	-4705	13.917	0.988
TZ	-542	-5653	16.87	0.966

Effect of parametric factors on adsorption studies

Effect of initial concentration

The results of the effect of concentration of the dyes is shown in Figure 1 and the percentage removal of tartrazine and methylene blue dyes was found to be 94.30 and 92.43 respectively. The result shows a general increase in percentage removal as the initial concentration of the dyes increase from (20-60 ppm) for both the single and binary phases. This increase in dye concentration is due to the fact that more dye molecules are available for adsorption by the adsorbent. Similar trend has been reported by Enenebeaku *et al* [15].

Effect of contact time

The effect of contact time is one of the vital factors considered when using batch adsorption system. It is important because it gives insight into the sorption process and provides information on the maximum time required for considerable adsorption to take place [16].

Figure 2 shows the result of the adsorption of tartrazine and Methylene blue dyes in wastewater. It is observed that the percentage removal of the dyes increased with time. The observed percentage removal trend was TZ>MB. The increase in the adsorption was gradual after some hours which implied that during the initial stage of adsorption, a large number of vacant sites were available for adsorption but after some time the surface sites were occupied hence difficulty in adsorption due to repulsive forces between the solute molecules on the adsorbent surface and the solution phase. Similar observations have been reported by some researchers [16, 17].

Effect of ionic strength

The ionic strength of a solution is a crucial parameter that controls both electrostatic and non-electrostatic interaction between the dyes and the adsorbent surface. Extensive investigations carried out on adsorption of dyes revealed that the extent of dye uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the dye bath [18].

The results of the percentage removal are presented in Figure 3. From the results, it is observed that the percentage removal of the tartrazine and methylene blue dyes decreased as the concentration of NaCl was varied from 0.02 – 0.10 M. These results can be explained as follows: The NaCl salt occupies the surface of the adsorbent sites before the dyes. Therefore, the surface of sorbent material becomes difficult for the dyes' uptake when the quantity of NaCl salt in solutions increase. The presence of salt inhibits the dyes uptake on surface of the adsorbent. Similar remarks have been proven by Bounmediene *et al* [14] who investigated the effect of pH and ionic strength of methylene blue removal from aqueous solution by sorption onto orange peel.

Effect of dosage

Adsorbent dosage is also a vital parameter in the adsorption of dyes owing to its effects on the amount of dyes removal per unit mass of the adsorbent.

Figure 4 has shown an increase in adsorption percentage of tartrazine and methylene blue dyes removal as the adsorbent mass increase from 0.5-2.5 g. The increase in the removal efficiency was more at 0.5 – 2.0 g and slight increase at 2.5 g for all the dyes in wastewater.

This increase is due to greater availability of exchangeable sites or surface area at the higher dose of the adsorbent. This corresponded with the results of other researchers [19, 20].

Effect of temperature

Temperature affects spontaneity, equilibrium, rate and randomness of the adsorption process. An increase in temperature can affect the adsorption process [21].

Figure 5 shows the result of the removal efficiency of tartrazine and methylene blue dyes. Increase in temperature from 30 -50 ^{o}C was found to result in decrease in removal efficiency of the dyes in solutions. The decrease in the adsorption process might be due to the weakening of the attractive forces between the adsorbent and the adsorbate ions. At high temperature the thickness of the boundary layer was expected to decrease due to the tendency of dyes to escape from the surface of the adsorbent to the solution phase. These observations are similar to those in the work by Kukwa *et al* [16].

Adsorption kinetics

A kinetic model helps in the study of adsorption rate and predict information about adsorbent/adsorbate interaction (physiosorption or chemisorptions) [22]. Pseudo first-order kinetic and pseudo second-order kinetic models were employed for adsorption kinetic behaviour of the adsorbates on the adsorbent. The accepted kinetic model for a given adsorption is based on three fundamental validity tests: A good and high correlation coefficient (R^2) indicating the applicability and reliability of a given model, a close agreement between the calculated and experimental q_e values and the accepted model must have the least values for the sum of error squares (%SSE), determined using equation below [23].

$$\%SSE = \sqrt{\sum \frac{(q_e exp - q_e cal)^2}{N}} \qquad (7)$$

Pseudo first and second order kinetics

Pseudo first order kinetics models is based on the assumption that the rate of adsorption is proportional to the number of vacant sites available on the adsorbent surface and is used regularly in liquid-solid phase [24]. Table 1 shows the experimental data tested for pseudo first order model. The conformity between experimental data and the model values was expressed by the coefficient of determination R^2. The R^2 values for tartrazine and methylene blue was found to be 0.983 and 0.986 respectively. These values show that the model has a good applicability and also explains the mechanism of adsorption kinetics. The Qexp and Qcal values for the dyes TZ and MB were 1.87, 1.85 and 1.45, 1.01 respectively. Qexp is the value

from the equilibrium capacity at the effect of time while Qcal is the value from the intercept of first order equation. The Qexp and Qcal values are close which implies a good fit for the adsorption.

The regression coefficient (R^2) for pseudo second order model also suggested the applicability of the kinetic model to describe the adsorption processes of dyes removal on the adsorbent [25].

Table 2 shows the regression coefficient R^2 of tartrazine and methylene blue to be 0.963, 0.999 respectively. These values indicate that the adsorption also follows second order and the model is applicable. The Qexp and Qcal values for the dyes TZ, MB are 1.86, 1.85 and 1.89, 1.96 respectively. These values are also much closer which implies that the adsorption also follow second order. The adsorption process is best fitted in Pseudo second order with the coefficient of determination (R^2) 0.999.

Thermodynamics studies

The thermodynamic parameters, such as Gibbs free surface energy change (ΔG^0), change in standard enthalpy (ΔH^0) and change in standard entropy (ΔS^0) define the feasibility of the adsorption process. From the Van't Hoff plot on Figure 8 and Table 3 the parameters were determined. The values of ΔG in KJ/mol for tartrazine and methylene blue were negative (-542 and -489). ΔH had -5653 J/mol for TZ and -4705 J/mol for MB while ΔS obtained was 13.92 for TZ and 16.87 for MB. The negative values of ΔH represent exothermic reaction. A positive value of ΔS reflects the affinity of the sorbent towards the sorbate, the increased randomness in the solid-liquid interface, increased the degree of freedom of the sorbate and more favourable condition for the occurrence of the adsorption process. The negative values of the ΔG reflect the spontaneous adsorption process [26].

CONCLUSION

Silica xerogel was extracted from rice husk and modified with nitric acid for adsorption. The adsorption of methylene blue and tartrazine were investigated under the effect of concentration, temperature, time, ionic strength and dosage and the adsorbent shows higher adsorption efficiency on the tartrazine removal as compared to methylene blue for all factors that were studied in the adsorption from wastewater. Pseudo second-order kinetic model described best the adsorption of the dyes onto silica xerogel based on the three validity test (good correlation values, closeness in q_e exp. and q_e cal. and small values of SSE%). The adsorption efficiency was achieved as well as the above objectives. The work was limited to simultaneous

adsorptionof methylene blue and tartrazine from simulated wastewater. More dyes especially industrial dyes should be considered in subsequent research for their adsorption. Adsorption by low cost adsorbent and biosorbents is recognized as an effective and economic alternative method for wastewater treatment.

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