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Comparative Studies on the Adsorption of Rhodamine B and Malachite Green from Simulated Wastewater onto Bentonite Clay

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ABSTRACT

Bentonite clay, a readily available adsorbent was employed in the investigation of the removal of synthetic basic dyes from simulated wastewater. Batch adsorption experiments were carried out for the sorption of the basic dyes, i.e. Rhodamine B and Malachite green onto the clay. The specific surface area (Sear's method), point of zero charge (Solid addition method) and functional groups present on the clay were determined using the Fourier Transform Infrared Spectroscopy (FTIR). The influence of process variables such as initial dyes concentrations, ionic strength, pH and contact time were also investigated. The isotherm equilibrium data were fitted to the linear forms of the Langmuir, Freundlich and Temkin isotherm models. The result of the Freundlich plots showed that both dyes were adsorbed onto a heterogeneous adsorbent surface with sorption capacities of Rhodamine B and Malachite green being 0.386 mg/g and 0.805 mg/g respectively. The data from the kinetic studies were fitted into the pseudo-first order, pseudo-second order and Boyd kinetic models. Over the study of these parameters, the pseudo-second order and film diffusion mechanism was found to predominate in the adsorption process of the dyes. Process variables such as pH and ionic strength was found to have a significant effect on the uptake of both dyes.

Keywords: Adsorbent, Adsorption, Fourier Transform Infrared Spectroscopy, Simulated, Synthetic

INTRODUCTION

The detoxification of wastewater in this present day in our environment is of grave concern. The discharge of dye effluents by the textile industries, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, distilleries, food companies, and a host of other industries generate and discharge this coloured wastewater directly into the surrounding water bodies which is undesirable as a result of the fact that the dyes drastically reduces the penetration of sunlight into the water body and hence diminishes reoxygenation in these receiving waters (McKay *et al.*, 1999). These coloured effluents are highly toxic to aquatic animals (Mittal and Venkobachar., 1989). Moreso, the discharge of these effluents, easily produce toxic trihalomethanes when chlorinated (Nakamura *et al.*, 2003). Most of these dyes can cause mutation in man, skin irrigation, are carcinogenic, recalcitrant and are highly resistance to biodegradation as they are highly resistant to heat and light (high thermal and photo stability) (Ho and McKay, 1998).

It was recently estimated that 12% of the synthetic dyes used per annum are lost during production and processing operations. 20% of these dyes also find their way into our environment through effluents that results from wastewater treatments (Weber and Stickney, 1993). The basic dyes are the class of dyes discovered to be brightest class of soluble dyes used in the industry with a very high tinctorial value (Hema and Arivoli, 2007). The availability of clean water for various activities is becoming the most challenging task for researchers and practitioners all over the world.

The two conventional methods for the treatment of coloured effluents are; the biological method and the physical/chemical method. Adsorption which is a physical/chemical method, is the method which has being mostly embarked upon amongst the various techniques available for dyes removal as it gives satisfactory results and can be used for different classes of colouring materials (Derbyshire *et al.*, 2001; Ho and Mackay, 2003; Jain *et al.*, 2003). One of the advantages of adsorption process over other methods is associated with its cost effectiveness and sludge free clean operation (Gupta and Suhas, 2009). Various researchers have engaged in the study of the possibilities of using inexpensive, non-conventional alternative materials as a result of the high cost associated with the production and regeneration of conventional adsorbents (Selvarani, 2000).

The removal of metal ions and dye molecules using bentonite clay over the last decade has gained more attention (Tahir *et al.*, 2010). This present study was embarked upon to investigate the efficiency of bentonite clay for the removal of these basic dyes in aqueous solutions and also taking cognizance of the difference in the chemistry of these dyes and the bentonite adsorbent.

MATERIALS AND METHODS.

Materials

Bentonite applied in this investigation was obtained from Integrated Mineral Technology Holdings Ltd. (IMT) Australia. It was used without further purification. Malachite green (MG) and Rhodamine B (RdB) were purchase from Sinopharm Chemical Reagent. All reagents used were analytical grades and they were used as received.

Adsorbent characterization.

The pH point of zero charge (pH_{PZC}) of the adsorbent was determined via the solid addition method as described by Balistrieri and Murray (1981). This was used to determine the pH at which the surface of the sorbent exhibits total surface electrical neutrality. The Sear's method (1956) was employed in determining the surface area of the adsorbent as well, as surface area is one of the major factors that affects adsorption processes. The surface functional groups present on the adsorbent and their possible involvement in the sorption process was examined from the FTIR (Buck Scientific Infrared Spectrophotometer, M-530) scanned between 400 – 4000 cm^{-1}.

Dye wastewater simulation and quantification.

The dyes used in this present work are; Malachite green, MG, (chemical formula = $C_{23}H_{25}N_2CI$, λ_{max}= 620nm) and Rhodamine B, RdB, (chemical formula = $C_{28}H_{31}CIN_2O_3$, λ_{max}= 543nm) were accurately weighed and dissolved in a double distilled-deionized water to prepare a stock solution (100 mg/L) and different working solutions which ranged between 2.5 mg/L – 30 mg/L were prepared from the stock via serial dilution.

Adsorption experiments.

The adsorption experiments were investigated using the batch method as described by Nidheesh *et al*. (2012). The adsorbent – adsorbate ratio was fixed at 0.1g of the adsorbent to 50 ml of the dyes solutions at every initial concentrations ranging from 2.5 mg/L to 30 mg/L. The mixture was capped in a conical flask and agitated on a temperature controlled magnetic stirrer at a constant speed of 1000rpm until equilibrium was attained. Samples were withdrawn after the equilibrium time (3hrs) and centrifuged at 4000rpm for 20mins for complete separation of the bentonite particles from the solution and the residual dye concentrations were calculated from the calibration curve. The kinetics of sorption of the dyes was studied by monitoring the uptake of the dyes from aqueous solution at different time intervals (1,3,5,10,20,30,60,90,120,180 mins) (Olaseni *et al*., 2014). The amount of dye adsorbed per unit mass of the adsorbent was calculated using equation (1);

$$q_e = \frac{(C_o - C_e)}{m} V \tag{1}$$

where C_o (mg/L) is the initial concentration of the dye, C_e (mg/L) equilibrium concentration, m is the mass of the adsorbent, and V is the volume of the solution. Percent dye removed (%DR) was calculated using equation (2);

$$\%DR = \left(\frac{C_o - C_e}{C_o}\right) X\,100 \tag{2}$$

Influence of pH.

The effect of pH was investigated between pH 4 to pH 12. The different pH (4-12) of the aqueous solution was adjusted by the addition of either 0.1M HCl or 0.1M NaOH solution via drop wise method when necessary to the dyes solutions before the introduction of the adsorbent. The adsorbent-adsorbate ratio was fixed at 0.1g to 50ml while the initial concentration was fixed at 30 mg/L.

Influence of Ionic strength.

The dyes solution ionic strength effect was also examined by using NaCl solution of varying concentrations; 0%, 0.1%, 0.5% and 1% (w/v) which is equivalent to ionic strengths of 0.0 mol/L, 0.017 mol/L, 0.085 mol/L and 0.17 mol/L (Oladoja *et al*, 2011). The adsorbent-adsorbate ratio was also fixed at 0.1g to 50 ml while the initial concentration was fixed at 30 mg/L.

Error Analysis.

To examine the best fit of the different kinetic models to the observed experimental data, an error function is required in the optimization procedure. In this study, the kinetic models were examined using the linear coefficient of determination, R^2, and the non-linear chi-squared statistical method, χ^2. The coefficient of determination R^2, represents the percentage of variability in the dependent variables that has been explained by regression line (Oladoja and Akinlabi, 2009). The value of the coefficient of determination may vary from zero to one and was calculated with the aid of equation (3);

$$R^2 = \frac{S_{xy}^2}{S_{xx} - S_{yy}} \tag{3}$$

Where S_{xx} is the sum of squares of x, S_{yy} is the sum of squares of y and S_{xy} is the sum of squares of x and y.

To evaluate the best of the kinetic models that fit the experimental data, the sorption process was also examined using nonlinear chi-squared (χ^2) statistical test. The chi-squared statistical test is basically the sum of the squares of the difference between the experimental data and the theoretical data obtained by calculating from models, with each squared difference divided by the corresponding theoretical data obtained by calculating from models. The equivalence of the mathematical statement is as presented in equation (4);

$$\chi^2 = \frac{\sum\left(q_{e.exp} - q_{e.theo}\right)}{q_{e.theo}} \qquad (4)$$

Where $q_{e.exp}$ is the experimentally obtained adsorptive capacity and $q_{e.theo}$ is the theoretically obtained (calculated) adsorptive capacity, which is the quantity of the material adsorbed per unit gram of the adsorbent (mg/g). If the data from model and experimental data are similar, then χ^2 value will be small and if they are different χ^2 will be a large value (Mahdi *et al*., 2012).

TABLE 1: Structure and properties of Rhodamine B and Malachite green

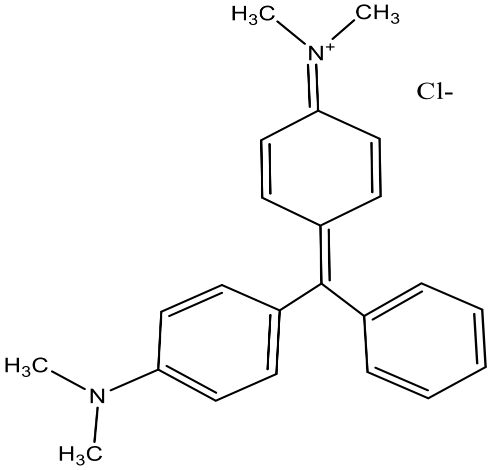
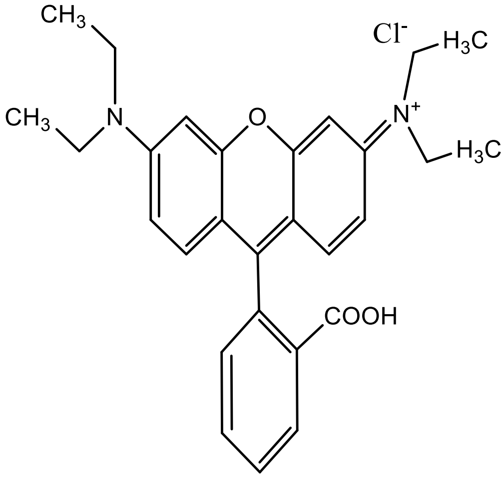
	Malachite green	Rhodamine B
Structure		
Molecular formula	$C_{23}H_{25}N_2Cl$	$C_{28}H_{31}N_2O_3Cl$
Molecular weight (g/Mol)	364.91	476.01
λ_{max}, (nm)	543	620

Table 2: Kinetic models for the adsorption of RDB and MG onto Bentonite.

Kinetic model	Linear form	Plot	Parameters	Ref.
Pseudo-first order	$\mathrm{In}(q_e - q_t) = \mathrm{In}q_e - K_1 t$	$\mathrm{In}(q_e - q_t)$ *vs t*	q_e, K_1	Lanregren (1889), Ho, (2004).
Pseudo-Second order	$\frac{t}{q_t} = \frac{1}{K_2}q_e^2 + \frac{1}{q_e}t$	$\frac{t}{q_t}$ *vs t*	q_e^2, K_2	Lin and Wang, (2009).

RESULTS AND DISCUSSION.

Adsorbent Characterization.

The functional groups present on the surface of adsorbents may alternate between the negative and positive charge states and this is informed by the pH of the system. The pH at which the surface of the adsorbents exhibits total electrical neutrality is known as the pH point of zero charge (pH_{ZPC}) (Khan *et al*, 2013). A large relationship is exhibited between the adsorbent and the amount of adsorbate adhered to its surface and the pH_{ZPC} of the adsorbent which; at pH values higher than the pH_{ZPC} when the surface of the adsorbent is dominated by negative charges, adsorption of positively charged adsorbates to the surface of the adsorbent will be highly favoured, while at pH value lower than the pH_{ZPC} when the surface of the sorbent is dominated by positive charges, adherence of negative charged adsorbates will be favoured (Nomanbhay and Palanisamy, 2005) The surface charge of bentonite employed in this study was determined and it was found that it possesses a pH_{ZPC} of 2.14 which was supported by literature to be between 2.0 and 3.0 (Hashen, 2012; Akpomie and Dawodu, 2015., Kosmulski, 2009) indicating that the sorbent is suitable for the removal of basic dyes over a large pH range above 2.14. The surface area of the bentonite used in this study was determined using the Sear's method as earlier described and it was found to possess a surface area of 21.5 (m^2/g). Shu-li *et al.* (2009) and Xifang *et al.* (2007) reported 20 (m^2/g) and 31.5 (m^2/g) respectively. The difference in these reported results could be ascribed to the methods of preparation, methods of determination, purity and type of bentonite. The FTIR analysis of the adsorbent surface before and after (raw and spent adsorbent) dyes adsorption was examined and presented in figure 1. From the analysis, the peak at 3456.80 cm^{-1} which is linked to the stretching vibration of H_2O, the peak at 1649.60 cm^{-1} is linked or corresponds to the bending of H_2O, the peak at 1047.20 cm^{-1} corresponds to the stretching of Si-O, the peak at 920.80 cm^{-1} denotes the bending vibration of Al-OH-Al. Furthermore, FTIR peak at 620.00 cm^{-1} is associated with Al-O + Si-O out of plane vibrations while the peak at 537.00 cm^{-1} denotes Al-O-Si vibration bending (Ekosse, 2005; Njoya *et al.*, 2006). Its noteworthy that the intensity of the peak at 1047.20 cm^{-1} observed in the spectra of bentonite (representing Si-O vibration) in the absence of adsorbed dyes (figure 1) considerably decreases after the dyes were adsorbed to its surface. A shift in the peak from 1047.20 cm^{-1} to 1046.40 cm^{-1} for malachite green and to 1052.80 cm^{-1} for Rhodamine B. This is attributed to the electrostatic attraction between Si-O group of the bentonite and the positively charged moiety present on the dyes (RdB and MG) indicating that there is possibility of the involvement of the Si-O group of the bentonite in the adsorption process while the shift in peaks is a pointer to the presence of adsorption.

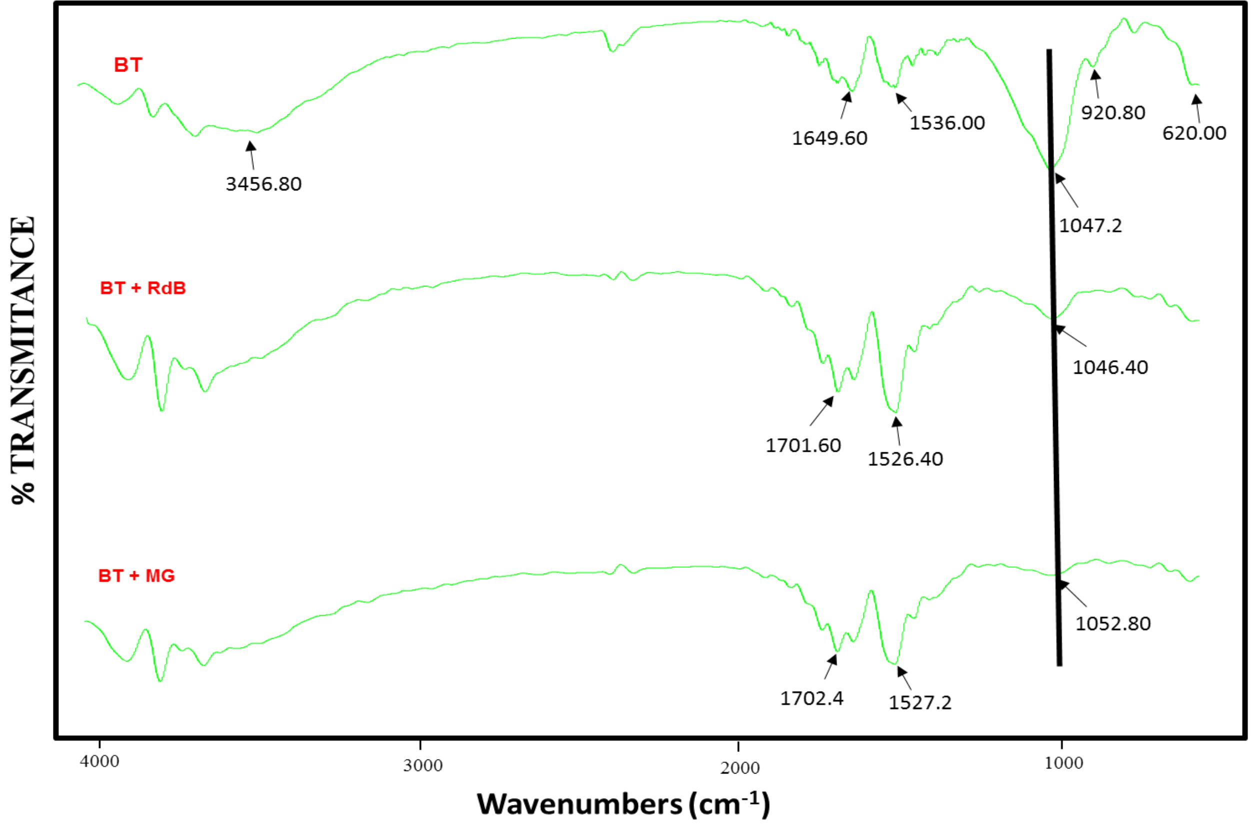


FIG 1: FTIR spectra of raw and spent bentonite clay.

Equilibrium isotherm Studies

The data obtained from the equilibrium isotherm studies were correlated to three isotherm equations: Freundlich, Langmuir and Temkin isotherm models. The Langmuir model assumes monolayer surface coverage on equivalent sites (Langmuir, 1918), The linear form of the Langmuir's isotherm model is expressed in equation (5);

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (5)$$

Where q_m the maximum value of adsorptive capacity (mg/g), K_L, is the Langmuir constant (L/mg) which is related to the energy of adsorption are obtained from the intercept and slope of the plot respectively (Alshabanat *et al*., 2013; Soni *et al*., 2012). The constants q_m and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e. The extremely poor correlation coefficient values (R^2) obtained from this model for both dyes indicates that the adsorption process did not occur via monolayer coverage of the adsorbent by the dyes. The important characteristics of the Langmuir isotherm, used to predict the efficiency of the adsorption, was expressed in terms of a dimensionless equilibrium parameter R_L, defined by $R_L = \frac{1}{1+K_L C_O}$, where C_o (mg/l) is the highest concentration of adsorbate. The value of R_L indicates if Langmuir isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0< R_L >1$) or irreversible ($R_L = 0$). The values of R_L at Co = 30mg/l in the present study were found to be 1.6058 X 10^{-3} for RdB and 0.718 for MG at 298.15 k, indicating that the adsorption of these basic dyes unto bentonite is favourable. Freundlich in 1906 published the first mathematical fit for adsorption isotherms which described the adsorption process unto a heterogeneous surface. Its linear form is expressed in equation (6);

$$\mathrm{Inq_e} = \mathrm{InK_f} + \frac{1}{\mathrm{n}}\mathrm{InC_e} \qquad (6)$$

Where q_e is the adsorptive capacity which is the quantity of the material adsorbed per unit gram of the adsorbent (mg/g), C_e is the equilibrium adsorbate concentration (mg/L); K_F, the Freundlich isotherm constant related to adsorption capacity (indicating the quantity of dye adsorbed onto the adsorbent) and n, the Freundlich isotherm constant related to adsorption intensity (which indicates the favourability of the adsorption process) can be obtained from the intercept and slope of the plot respectively (Freundlich 1906; Runping *et al*., 2008). Therefore, the plot of $\mathrm{Inq_e}$ versus $\mathrm{InC_e}$ gave a straight line of slope 1/n and intercepts $\mathrm{InK_f}$. The high value of the correlation coefficient ($R^2 = 0.980$ for RdB and 0.905 for MG) indicates that the process occurred via heterogeneous coverage of the adsorbent surface. The values of K_F which denotes the sorption capacities of the adsorbent towards the dyes was found to be 0.386 mg/g for RDB and 0.8055 mg/g for MG. The linear form of the Temkin isotherm model which is based on the assumption that the free energy of adsorption is dependent on the surface coverage and takes into account the interactions between adsorbents and dye molecules is given in equation (7);

$$q_e = \mathrm{BInA_T} + \left[\frac{\mathrm{RT}}{b_T}\right]\mathrm{InC_e} \qquad (7)$$

Where: A_T is the equilibrium binding constant [L/g], b_T is the adsorption constant [J/mol K], R is the universal gas constant (8.314 J/mol K), T is absolute temperature value [298 K], B is a constant related to the heat of sorption [J/mol]. The Temkin isotherm model display a correlation coefficient values of 0.899 for RdB and 0.754 for MG which are lower than those observed from the Freundlich isotherm model as shown in Table 3. Therefore, the Temkin isotherm model do not describe the mechanism of sorption of these dyes unto bentonite.

TABLE 3: Adsorption isotherm Analysis

Isotherm model	Parameters	Rhodamine B	Malachite green
	R^2	0.465	0.042
Langmuir	K_L (dm^3/mg)	20.689	0.013
	q_m (mg/g)	9.434	55.556
	R^2	0.980	0.905
Freundlich	K_F (mg/g)	0.386	0.805
	N	0.732	0.987
	R^2	0.899	0.754
Temkin	B (J/mol)	4.457	3.758
	A_T (L/g)	0.612	0.894
	b_T (J/molK)	555.880	659.279

Effect of pH on the adsorption process.

The influence of pH on adsorption processes cannot be over emphasized in an adsorption process as the pH of the system greatly influences the charges (net charge) on the surface of the adsorbent, the extent of dissociation of the functional groups present on the adsorbent and hence its sorption capacity for the adsorbate (Nandi *et al*, 2009).

The result of the influence of pH on the adsorption of RdB and MG are presented in Figure 2. From the plots it is evident that the initial pH of the system played a significant role in determining the level of adsorption. It was observed that the maximum percentage of the dyes removed was at pH 4 (over 70% for RdB and over 90% for MG) and thereafter reduced in a steady manner to pH 12. This variation in behavior of the adsorption can be explained on the basis of point of zero charge of the adsorbent (pHZPC = 2.14) as well as the structures of the dyes. At pH below the point of Zero charge of the adsorbent (2.14) the surface of the sorbent has a high positive charge density and under this condition, the uptake of positively charged dyes would be low. With increasing pH i.e. beyond the point of zero charge, negative charge density on the surface of the adsorbent increases, resulting in an enhancement in the removal of these positively charged dyes. Also as a result of the acidic groups on these dyes that dissociates with increasing pH, giving rise to negative charge on the dyes which accounts for the reduction in the percentage removed in these dyes at higher pH. The difference in the percentage removals observed in the dyes is attributed to the presence of the acidic group (-COOH-) present in RdB but absent in MG. The presence of this group increases the negative charge density of the dye (RdB) and hence increasing the level of repulsion between the dye and the surface of the adsorbent which is already dominated by negative charges.

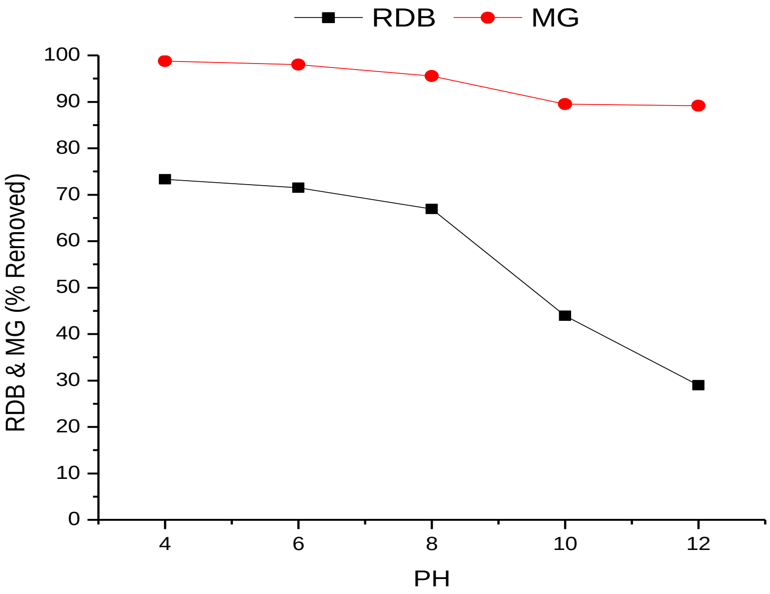


Fig 2: Percentage removal of RdB and MG onto bentonite at different initial pH values and a constant concentration of 30 mg/L for each dye.

Influence of Ionic Strength.

Ionic strength of a system is one of other major factors that affects adsorption rate as it influences the level of electrostatic attraction or repulsion between adsorbates and adsorbents and these ions also compete with the adsorbate ions for the active sites present on the adsorbents. The major importance of the study of the influence of ionic strength is to examine the existence of the hydrophobic – hydrophobic interactions which is the attraction between the nonpolar groups of the dye and the adsorbent (Muhammad and Linda, 2015). From the result presented in Figure 3, it can be observed that an increase in ionic strength (0 - 0.17 mol/L) of the solution led to an increase in the total percentage of the dyes that were removed as compared to the solution without the salt (NaCl). This confirms that hydrophobic – hydrophobic and Coulombic interactions may be the dominant attraction force for the RdB and MG - bentonite adsorption system. A similar case of this type of interaction was reported by Mohammad and Linda (2016), for the removal of RdB dye from aqueous solution using *Cauarina Equisefolia* Needles (CEN).

In solution of high ionic strength, the mechanism of electrostatic attraction is suppressed due to the effect of the competition between the cationic dyes and the Na^+ present for the active sites on the surface of the adsorbent. Hydrophobic – hydrophobic interaction is enhanced under high ionic strength conditions by the electrical double layer that brings particles closer together being compressed which in turn leads to increase in dye adsorption. as observed in Figure 3. Hu *et al* (2013), also reported a similar observation for the sorption of methyl orange, methylene blue and neutral red by resins.

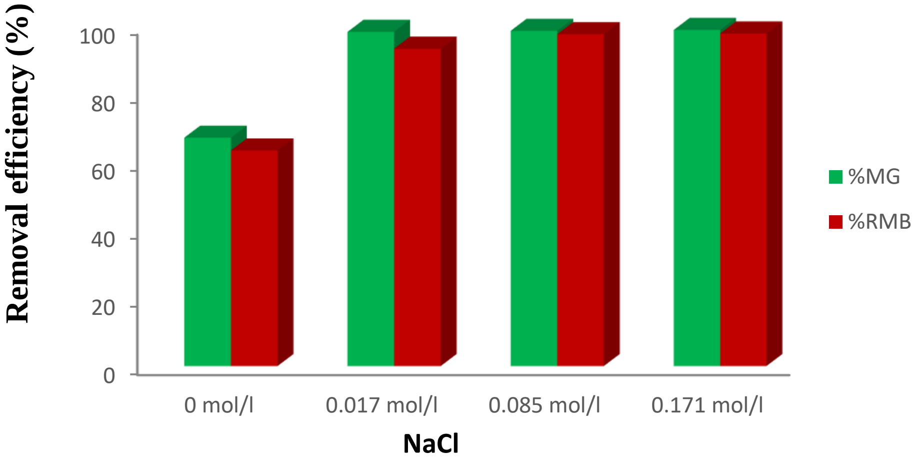


Fig. 3: Effect of Salt on the Adsorption of RdB and MG onto Bentonite at the Initial dye concentration of 30 mg/l.

Adsorption kinetic studies.

The adsorption kinetics of RdB and MG onto the surface of bentonite was monitored using the Pseudo-first and Pseudo-second order kinetic models whose linear forms are presented in Table 2. In cases where the adsorption process occurred via diffusion through the boundary layer, the process must have followed the pseudo-first order mechanism, but in cases where the film diffusion mechanism predominates, the process followed the pseudo-second order mechanism (Oladoja and AKinlabi, 2009). As observed from Tables 4 and 5, the poor correlation coefficient (R^2) values of the pseudo-first order kinetic model and extremely high larger values for the chai-squared (χ^2) (which was informed by the large difference between the calculated q_e values and experimental q_e values) is a pointer to the fact that the pseudo-first order kinetic model cannot be used to describe the adsorption process, indicating that the process did not occur via diffusion through the boundary layer for both dyes. The pseudo-second order kinetic model on the other hand as observed from Tables 6 and 7, possesses correlation coefficient values close to unity (1) for all initial concentrations investigated for both dyes, and also the negligible values of the statistical chai-squared values (χ^2) (informed by the negligible difference between the calculated q_e and experimental q_e) confirms that the adsorption process follows the pseudo-second order kinetic model for both dyes, indicating that the process occurred via film diffusion mechanism. From Tables 6 and 7 it was also observed that the values of the initial sorption rate (h), amount of dyes sorbed at equilibrium (q_e) increased with increasing initial concentrations for both dyes while the pseudo-second order rate constant K_2 decreased with increasing initial concentrations. Muhammad and Linda (2015; 2016), had also reported the mechanism of Rhodamine B and Malachite green to have occurred with the pseudo-second order mechanism.

Table 4: Pseudo-first order kinetic parameters for the adsorption of RdB onto bentonite.

Conc (mg/l)	R^2	K_1 (min^{-1})	$q_{e(exp)}$(mg/g)	$q_{e(theo)}$(mg/g)	χ^2
2.54	0.976	0.022	0.5368	0.092	2.1505
5.01	0.812	0.021	1.3968	0.041	44.8075
9.86	0.911	0.018	2.8951	0.122	63.0335
15.1	0.941	0.025	4.5514	0.379	45.9338
32.25	0.947	0.414	10.2264	0.528	178.1419

Table 5: Pseudo-first order kinetic parameters for the adsorption of MG onto bentonite

Conc (mg/l)	R^2	K_1 (min^{-1})	$q_{e(exp)}$(mg/g)	$q_{e(theo)}$(mg/g)	χ^2
2.2	0.884	0.019	0.8022	0.266	1.080866
4.96	0.91	0.019	1.0902	0.576	0.459031
9.04	0.871	0.022	3.584	1.592	2.492503
15.11	0.994	0.023	6.4953	2.081	9.363789
31.43	0.884	0.021	11.4441	4.829	9.061824

Table 6: Pseudo-Second order kinetic parameters for the adsorption of RdB onto bentonite.

Conc (mg/l)	**R^2**	**h (min^{-1})**	**k_2 ($gmg^{-1}Min^{-1}$)**	**$q_{e(exp)}$(mg/g)**	**$q_{e(theo)}$(mg/g)**	**χ^2**
2.54	0.999	0.351	1.212	0.5368	0.563	1.20×10^{-3}
5.01	1	6.306	3.224	1.3968	1.395	1.41×10^{-6}
9.86	1	7.692	0.916	2.8951	2.892	3.32×10^{-6}
15.1	1	7.353	0.353	4.5514	4.551	3.52×10^{-8}
32.25	1	33.333	0.314	10.2264	10.292	4.18×10^{-4}

Table 7: Pseudo-Second order kinetic parameters for the adsorption of MG onto bentonite.

Conc (mg/l)	**R^2**	**h (min^{-1})**	**k_2 ($gmg^{-1}min^{-1}$)**	**$q_{e(exp)}$(mg/g)**	**$q_{e(theo)}$(mg/g)**	**χ^2**
2.2	0.998	0.205	0.316	0.8022	0.789	2.21×10^{-4}
4.96	0.996	0.13	0.104	1.0902	1.064	6.45×10^{-4}
9.04	0.998	0.607	0.045	3.584	3.543	4.47×10^{-4}
15.11	0.999	1.748	0.040	6.4953	6.444	4.08×10^{-4}
31.43	0.998	2.179	0.016	11.4441	11.293	2.02×10^{-3}

Boyd Kinetics

To actualize the rate controlling mechanism involved in the adsorption of RdB and MG onto the surface of bentonite, the sorption kinetic data were further examined using the Boyd kinetic model (Boyd *et al.*, 1947), according to equation (8)

$$\mathrm{F} = 1 - (6/\mathrm{t}\pi^2)\exp(-\mathrm{B_t}) \qquad (8)$$

Where B_t represents the mathematical function of F, and F is the solute adsorbed fraction at various time t. F can be defined using equation (9)

$$F = \frac{q_t}{q_\infty} \qquad (9)$$

Where q_t is the amount adsorbed at time t, q_∞ represents the amount adsorbed at infinite time. (In this study is 180min). A linear form of the Boyd kinetics is written in equation (10):

$$\mathrm{B_t} = -0.4978 - \mathrm{In}(1 - \mathrm{q_e}/\mathrm{q_t}) \qquad (10)$$

Hence, the values of B_t can be estimated for each value of F using equation 10. The calculated B_t values were plotted against time (Figures 4 and 5), and the linearity test of the B_t versus t plot for different initial RDB and MG concentrations was employed to differentiate between the particle diffusion and film diffusion controlled adsorption process. If the Boyd plot is a straight line passing through the origin (zero intercept), the particle diffusion mechanism predominates, however, if the plots do not pass through the origin (i.e. intercept greater or less than zero), the film diffusion mechanism predominates (Boyd *et al.*, 1947). Figure 4 and Figure 5 shows that the Boyd plots for the removal of RdB and MG by Bentonite do not pass through the origin, indicating that the film diffusion mechanism predominates in the adsorption process. This further supports the pseudo-second order kinetic model observed in the adsorption kinetics earlier discussed.

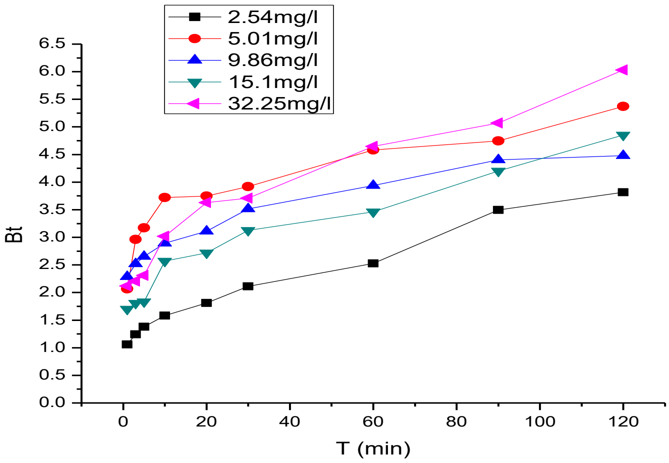


FIG 4: Boyd kinetic plot for the sorption of RdB onto Bentonite at different initial concentrations.

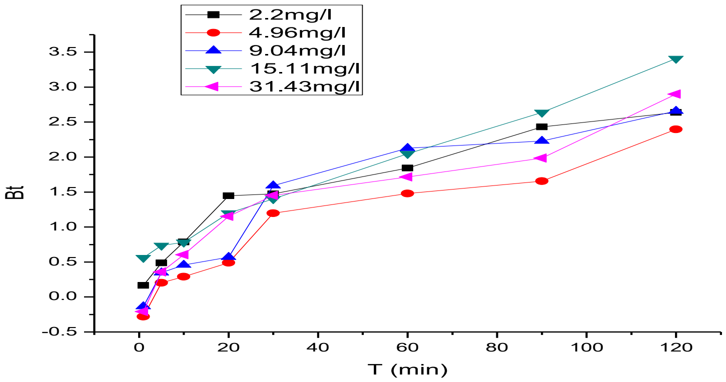


FIG 5: Boyd kinetic plot for the sorption of MG onto Bentonite at different initial concentrations

CONCLUSION

This present study evaluated the efficiency of readily available low cost adsorbent (Bentonite) for the decolourization of a simulated wastewater contaminated with basic dyes (RdB and MG). The adsorbent was characterized for its surface area, point of zero charge and its available surface functional groups for the raw and spent bentonite. The efficiency of the adsorbent for the dyes was found to be influenced by the different optimized experimental conditions including change in pH, initial dye concentrations, ionic strength and contact time. The adsorbent in this study was found to possess a high adsorption potential for MG than its counterpart RdB and this phenomenon can only be attributed to the presence of the acidic group (-COOH-) attached to the RdB. This group enhances the electrostatic repulsion between RdB and the surface of the bentonite, hence the observed difference in the percentage removal for both dyes, i.e. at temperature of 298K and pH of 4, 98% of MG and 73% of RdB. The experimental data was tested against results of the kinetic and isotherm studies also revealed that the removal of the dyes were best fitted to the pseudo-second order model where the film diffusion mechanism predominated and Freundlich models, respectively.

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