



Adsorption of Methyl Orange from Aqueous Solution using Chitin and Polystyrene-Modified Chitin: Kinetics and Isotherm Studies

Abdulganiyu Umar

Department of Chemistry, Faculty of Science, Yusuf Maitama Sule University, Kano

*Correspondence Email: abdulg.ag@gmail.com

ABSTRACT

Chitin is a natural, biodegradable and non-toxic biopolymer. Batch adsorption experiments were conducted to remove methyl orange from aqueous solution. The influence of physicochemical parameters, such as solution pH, dye concentration, adsorbent dosage and contact time were investigated. The results showed that the modified chitin has improved adsorption capacity and the percentage dye removal strongly depends on pH, nature and structure of the dyes. The maximum adsorption of methyl orange by both raw chitin and polystyrene-modified chitin occurred at the pH of 6, with percentage dye removal of 26.38% and 35.20% respectively, for an initial concentration of 10 mg/L. The pseudo-first-order model gives poor fittings for both chitin and the modified chitin as indicated by the low coefficients of determination (R^2). The pseudo-second-order model fits the experimental data well, having R^2 close to unity. The Langmuir isotherm was found to conform better than the Freundlich model in the adsorption of both dyes on both chitin and the modified chitin with R^2 of nearly unity.

Keywords: Adsorption, Chitin, Isotherms, Kinetics, Methyl orange, Modified chitin

INTRODUCTION

Environmental pollution has become a major concern of the 21st century due to human activities. It is well known that water is a vital natural resource for sustainable ecosystem. Dyes are water pollutants which are generally present in the effluents of leather, textile, paper and dye manufacturing industries. The high level production and extensive use of dyes worldwide generates coloured wastewaters even at low concentrations, resulting in water pollution (Dawood and Sen, 2012). The coloured dye effluents are generally considered to be toxic to the aquatic biota, as they exhibit high colour and high chemical and biochemical oxygen demands (COD and BOD) (Yao *et al.*, 2009). This also affects the symbiotic process by distorting the natural equilibrium via reduced photosynthetic activity as a result of coloration of water in rivers and streams (Bhatnagar and Sillanpää, 2009). Therefore, the removal of colour from wastewater is even more important than the removal of the soluble colourless organic substances.

Azo dyes account for 60-70% of all the dyes used commercially and they are the most problematic compared to other forms of dyes. This is because, they do not undergo aerobic degradation but instead decomposed under anaerobic conditions to produce colourless aromatic amines that cause allergic reaction, dermatitis, skin irritation and are potential carcinogenic (Dawood and Sen 2012; Bhatnagar

and Sillanpää 2009). Therefore, there has been considerable interest on the removal of such dyes from the wastewater.

Different techniques have been widely used for the treatment of dye-bearing wastewater, such as chemical, physical and biological techniques, including biosorption, coagulation or flocculation, ozonation, advanced oxidation, membrane filtration (Yao *et al.* 2009, El-Latif *et al.*, 2010 and Ghaedi *et al.*, 2011). Adsorption is considered as the most effective techniques for the removal of dyes from wastewater due to its simplicity, ease of operation, cost effective and its non-sensitivity to toxic substances (Yao *et al.*, 2009, El-Latif *et al.*, 2010). Several materials have been used as adsorbent, but their cost ineffectiveness and non-biodegradability limits their applications, e.g. activated carbon, synthetic resins and silica.

Chitin and its modified forms have been used as adsorbents to remove dyes from wastewater. Chitin was used to remove Acid Blue 25, Acid Blue 158, Mordant Yellow 5 and Direct Red 84 (Mckay *et al.*, 1982). Adsorption of anionic dyes, orange IV, orange G, xylenol orange onto powdered chitin was reported (Longhinotti *et al.*, 1998). Another research group used chitin to remove indigo carmine (IC) and tyran blue (TB) dyes (Akkaya *et al.*, 2009). Chitin powder was used as bioadsorbent for the removal of ponceau-S dye from the aqueous solution (Shirsath and Shrivastava, 2012). Polystyrene was used as ion-

exchanger to remove SPADNS azo dye from aqueous solution (Greluk and Hubicki 2009). The removal of selected acid and basic dyes using some chitin derivatives was reported (Aly *et al.* 1997). Poly(acrylic) acid-modified chitin was used to remove some dyes in aqueous medium indicating its potential in wastewater treatment (Huang *et al.*, 2012). Methacrylic acid-modified chitin was used for the removal of paraquat from aqueous solution (Hsu *et al.*, 2013). Chitin obtained from shrimp shells was also used as adsorbent for the removal of crystal violet dye in aqueous solution (Khedr *et al.*, 2013).

In this study, we report the use of prepared chitin-g-polystyrene copolymer as adsorbent for the removal of methyl orange from aqueous solutions.

MATERIALS AND METHODS

Adsorbates and other Reagents

Chitin was purchased from Sigma Aldrich (USA). The Polystyrene-modified chitin was used as reported by Abu Naim *et al.* (2013). Methyl orange (MO) dye was used without further purification to prepare the aqueous solutions. Stock solutions of 1000 mg/L were prepared by dissolving 0.01 g of the dye in deionised water and made up to mark in a 10 cm³ volumetric flask. Experimental solutions were prepared by withdrawing an aliquot of the stock solutions and diluting them with deionised water. The pH values of the required concentrations were adjusted (using a Denver pH 700, pH meter obtained from Cole Palmer (Illinois, USA) by addition of either 0.1 M HCl or 0.1 M NaOH solution. All glassware and sampling bottles were cleaned, and then rinsed with deionised water and dried in an oven at 60°C.

The concentrations of the residual dyes were measured using UV-Visible spectrophotometer at a λ_{\max} corresponding to the maximum adsorption for the dye solution (λ_{\max} = 505.00 nm for MO). A calibration curve of the dye was obtained by plotting graph of its absorbance against concentration.

EXPERIMENTAL

Determination of Dye Calibration Curve

To determine the calibration curve of the dye used, dye solutions at different concentrations (20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L) were prepared (in 25 cm³ volumetric flasks) from the stock solution (1000 mg/L). The dye concentrations were evaluated using UV-Visible spectrophotometer (Perkin Elmer, LAMBDA 35) with quartz cell of 1 cm length for determining the absorbance at λ_{\max} of methyl orange at 505.00 nm dye concentration. A calibration curve was determined by plotting graph of absorbance against concentration.

Effect of pH on the Adsorption

To determine the best pH that will give maximum adsorption of methyl orange by the

adsorbent, pH values from 2 to 7 were prepared. The required pH solutions were adjusted by adding few drops of either 0.10 M HCl or 0.10 M NaOH solution. The adsorbents (20 mg) were mixed with 25 cm³ (40 mg/L) dye solutions (of different pH values) prepared from the stock solution (1000 mg/L). The mixtures were stirred with a bar magnet for 10 min at room temperature (298°C). The mixtures were then centrifuged at 4000 rpm for 20 min. UV-Visible spectrophotometer was used to record the remaining dye concentrations in the supernatants. The procedures were recorded in triplicates.

Effect of Dye Concentration on the Adsorption

The effect of this parameter on the adsorption was determined by preparing 10 cm³ dye solutions of different concentrations, ranging from 20 mg/L to 100 mg/L. To the 50 cm³ flasks containing above solutions was added a fixed amount of the adsorbents at a fixed optimum pH adjusted by adding few drops of either 0.10 M HCl or 0.10 M NaOH. All experiments were conducted at room temperature with constant stirring, using bar magnet stirrer. UV-Visible spectrophotometer was used to determine the remaining dye concentrations of the supernatants. The procedures were also recorded in triplicates.

Effect of Adsorbents Dose on the Adsorption

To the different conical flasks (50 cm³) containing 25 cm³ of 40 mg/L dye solutions with a fixed pH at optimum value, different amounts of adsorbents (20 mg, 40 mg, 60 mg, 80 mg, 100 mg, 120 mg and 140 mg) were added. All experiments were conducted at room temperature for 10 min with constant stirring using bar magnet. UV-Visible spectrophotometer was used to determine the remaining concentrations of the supernatants.

Effect of Contact Time on the Adsorption

Another vital parameter that could reveal the adsorption equilibrium in kinetic study is time. To the 50 cm³ conical flasks containing fixed amounts of the adsorbents at optimum value, 25 cm³ dye solutions of fixed concentration (mg/L) at a fixed optimum pH value was added. The reaction mixtures were stirred (using bar magnet) at various times (1 min, 2 min, 3 min, 5 min, 7 min, 9 min and 11 min, 13 min and 15 min). The experiments were conducted at room temperature. After the adsorption at a given time, the supernatants were analysed using UV-Visible spectrophotometer to determine the remaining concentrations of dye solutions.

ADSORPTION STUDY

Adsorption study was conducted using batch method. The equations 1 and 2 adopted from Lin and Zhan (2012) were used to determine the

percentage of the dye adsorbed and amount of dye adsorbed at a time t , q_t (mg/g) by the adsorbents.

$$R_{ad} (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where R_{ad} is the percentage of the dye adsorbed, C_i is the initial concentration of dye (mg/L) and C_e is the residual (equilibrium) concentration of dye (mg/L).

$$q_t = \frac{C_i - C_e}{M} \times V \quad (2)$$

where q_t is the dye adsorbed onto unit weight of adsorbent, (mg/g), M is the adsorbent dose (g) and V is the volume of dye solution (L).

Similar experiments were repeated by using polystyrene-modified chitin (MCH) to

compare the amount of adsorption q_t (mg/g) and the percentage dye removal between raw and MCH.

RESULTS AND DISCUSSION

Fourier Transform Infra-Red Analysis

To ascertain the presence of polystyrene peaks in the prepared polystyrene-modified chitin copolymer (MCH), the FTIR spectra of raw chitin (RCH) and the modified chitin (MCH) were run and compared. Fig. 1 shows FTIR spectra of (a) RCH and (b) the MCH. The spectrum (b) indicate the presence of polystyrene peaks with IR-band intensities at 3150-3000 cm^{-1} (=C-H (aromatic)), 3000-2850 cm^{-1} (-C-H stretching (alkane)), 1660-1500 cm^{-1} (C=C aromatic) in addition to those of raw chitin at 3600-3200 cm^{-1} (O-H and N-H stretching) and 1659 cm^{-1} due to C=O stretching and this could enhance the porosity of the chitin.

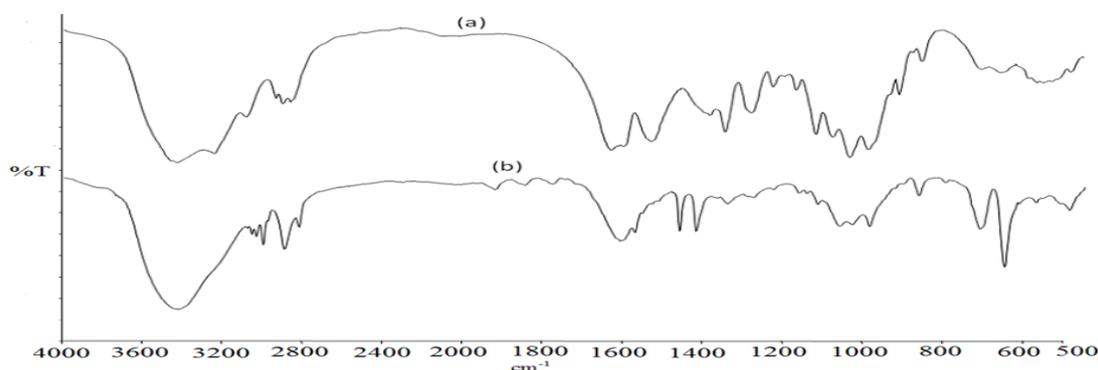


Fig. 1: FTIR Spectra of (a) RCH and (b) MCH

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images of the RCH and MCH are shown in Fig. 2(a) and 2(b), respectively. Although both adsorbents possess substantial number of porous sites, the porosity and texture of the MCH is larger than that of the RCH, even with magnification of

up to 25,000 for the raw chitin as shown in Fig. 2(a) and 2(b).

This increase in texture and porosity of the MCH could result to increase its adsorption capacity by trapping the dye molecules easily via pore diffusion during the adsorption process. This phenomenon was also reported by Tunali & Akar (2006).

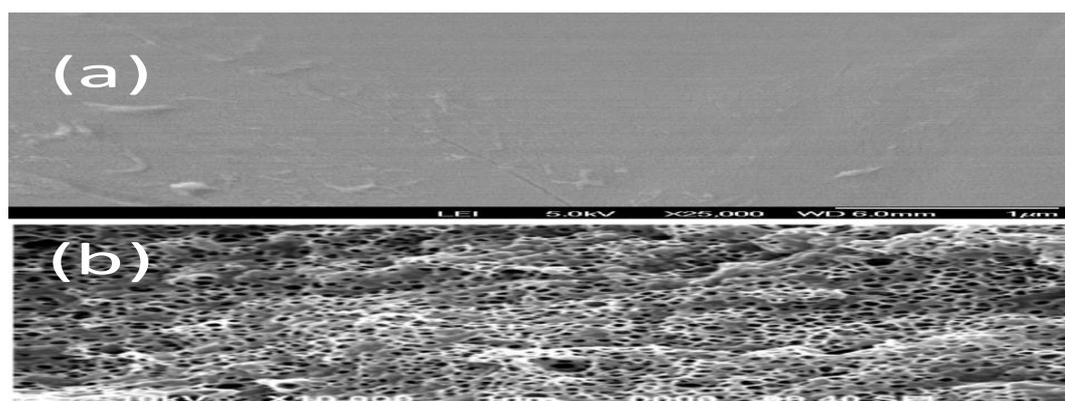


Fig. 2: SEM images of (a) RCH at 25,000 magnifications and (b) MCH at 1000 magnification

Effect of solution pH on Removal of Methyl Orange

The effect of different solution pH on the adsorption of MO by raw chitin (RCH) and polystyrene-modified chitin copolymer (MCH) were investigated in the pH range 2-7 and the results are shown in Fig. 3. The results showed that the adsorption capacity of both the RCH and MCH were pH dependent. Both biopolymers have OH (with small amounts of NH₂ found in chitin) functional groups. Since the studies were carried out in acidic media and neutral, it is expected that in acidic medium both OH and NH₂ will be protonated. The hydroxyl groups in particular, will be heavily hydrated, as such, will be basically unable to form hydrogen bonds with dyes; but the dyes could be adsorbed either via van der Waals interactions or by ion exchange with other groups (Giles and Hassan, 1958).

The results for the adsorption of MO by both RCH and MCH were found to be at optimum values at pH 6, as shown in Fig. 3. The figure

showed that there was an increase in percentage removal of MO by MCH from pH 2 to pH 6 (having 43.32%) in comparison to RCH alone (with 23.73%). This indicates that the MCH is more effective (as it has more adsorptive power) than RCH itself. This could be attributed to some reasons. Firstly, the MCH has larger BET surface area (12.4745 m²/g) compared to that of RCH (4.9183 m²/g) as shown in Table 1. Secondly, although the polystyrene has no functionality, yet, its porosity would promote intra-particle diffusion, which could enhance the adsorption process (by trapping the dye molecules) (Greluk and Hubicki, 2009). There was increased percentage of dye removal with increase in pH from 2-6, and then it decreased abruptly. At pH less than or equal to 2, there was very little or no adsorption. This could be due to the competition between other anions in the solution and the anionic dyes towards the densely positive charges on the surface of the adsorbent. (Longhinotti *et al.*, 1998).

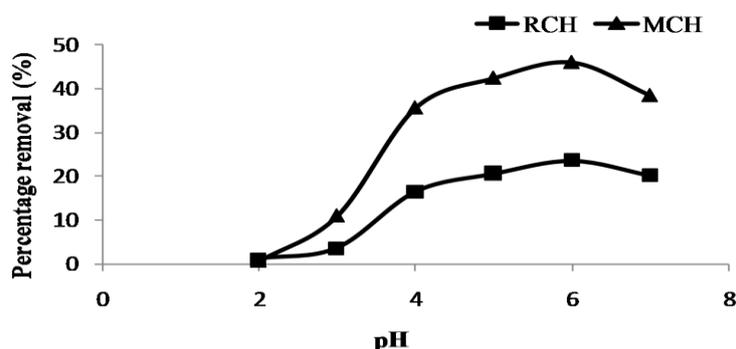


Fig. 3: Effect of pH on the percentage removal of MO by RCH and MCH

Effect of Adsorbent Dosage

The effect of adsorbent dosage of the RCH and MCH on the percentage dye removal of methyl orange (MO) were compared as shown in Fig. 4 and Fig. 5 respectively. It was observed that, at fixed dye concentration, an increase in the amount of the adsorbent from 20 mg to 140 mg resulted in an increase in the percentage removal of MO from 13.42% to 26.52%, for RCH and from 14.20 to 43.96% for MCH respectively, as shown (Fig. 5). The percentage removal of the dye reached equilibrium state at 120 mg. Further increase in the amount of adsorbent was found to have no significant effect on the percentage dye removal, indicating that the complete dye removal could not be achieved by using large amount of the adsorbent.

It should also be remembered that, the polar functional groups of the adsorbent played a vital role in binding the dye molecules to the

surface of the adsorbent via van der Waals forces, during the adsorption process (Malik *et al.*, 2007). Thus, the increase in percentage dyes removal at a fixed dye concentration could be due to the affinity of MO toward easily accessible pores, functional groups and surface area per unit mass of the RCH and its MCH form. Similar observations were reported in the removal of malachite Green and other related basic dyes (Hameed and El-Khaiary, 2008; Pan and Zhang, 2009; Sharma *et al.*, 2009; Bekçi *et al.*, 2008; Bekçi *et al.*, 2009).

The decrease in the percentage dye removal with increase in the adsorbent dosage at fixed dye concentration could be either due to the split in a flux or the concentration gradient between the dye concentration in the solution and the concentration of the dye on the surface of the adsorbent, leading to decrease in the amount of the dyes adsorbed onto unit mass of the adsorbent (Dawood and Sen, 2012).

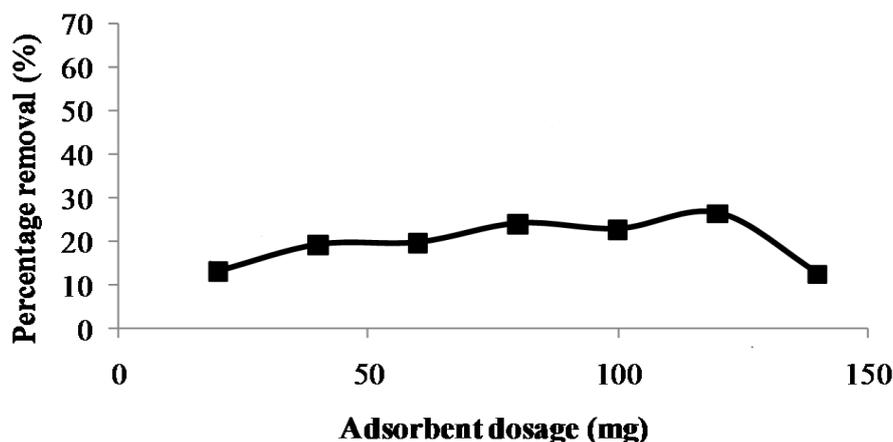


Fig. 4: Effect of RCH Dose on Percentage Removal

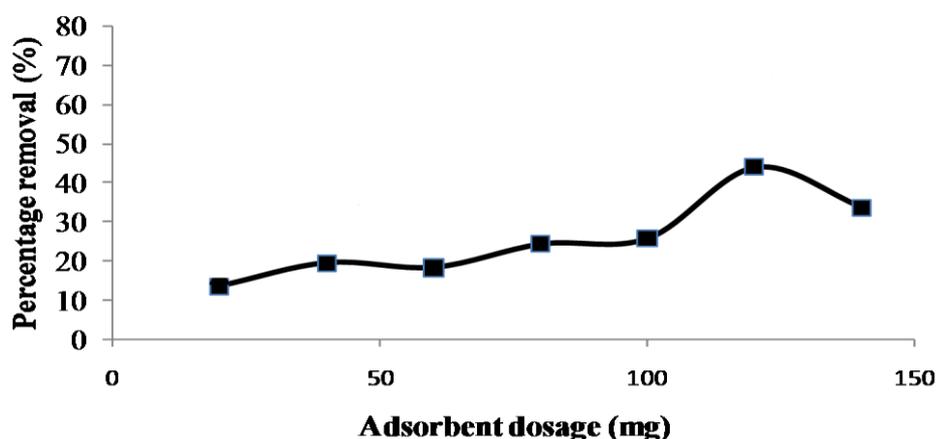


Fig. 5: Effect of MCH Dose on Percentage Removal

Effect of Contact Time

The effect of contact time on the percentage removal of MO by RCH and MCH were studied using 40 mg/L (10 cm^3) of dye, 120 mg adsorbent dose for dye solution and solution pH 6 as shown in Figs. 6 and 7. The percentage dye removal (%) was found to increase with time, and the figures showed that, the percentage dye removal by RCH was found to be 16.56%. There was a rapid percentage dye removal in the beginning from 1 to 2 min for the dye, indicating the affinity of the adsorbate toward adsorbents by directing their functional groups (SO_3^-) to the positively charge sites of the adsorbent. The adsorption continues infinitesimally slowly, then

decreased after 11 min with 16.56% and that of the MCH 40.36% respectively.

The rapid percentage dye removal of the dye in the beginning of the adsorption process could be due to the availability of large amount of vacant adsorptive sites in the adsorbent. The infinitesimal increase in the percentage dye removal was observed with decrease in the number of available adsorptive sites in the adsorbent, until the sites are saturated. (Hameed and Ahmad 2009). The gradual decrease in the percentage dye removal could be due to the split in a flux or the concentration gradient between the dye concentration in the solution and the concentration of the dye on the surface of the adsorbent at longer contact time (Dawood and Sen 2012).

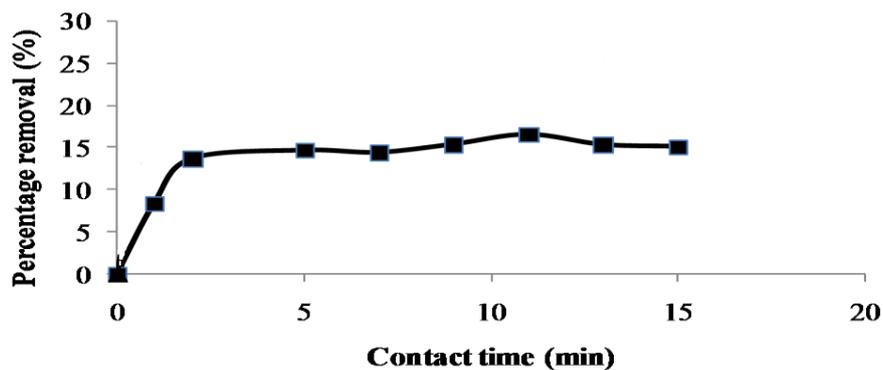


Fig. 6: Effect of contact time on the percentage removal of MO by RCH

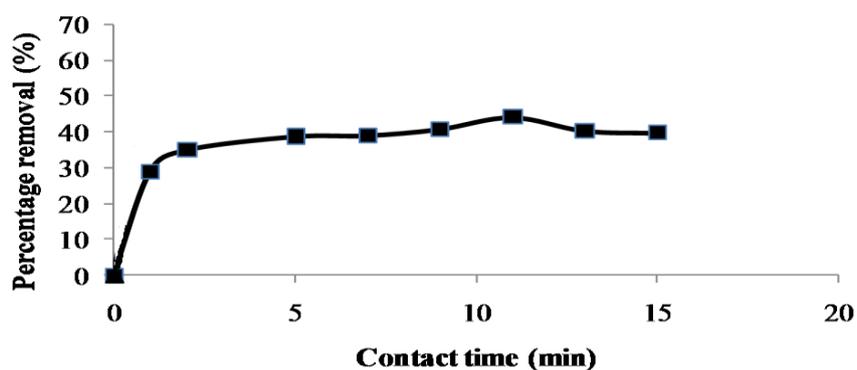


Fig. 7: Effect of Contact Time on Percentage Removal of MO by MCH

Effect of Initial Dye Concentration

The percentage removal of the dye showed a decreasing trend with increase in the dye concentration as shown in Fig. 8 and Fig. 9. It was found that the percentage removal of MO using both modified chitin and raw chitin increased from 11% to 35.20% and 14.98% to 26.38%,

respectively. It is assumed that, at lower concentration, there would be maximum interaction between the dye molecules and the binding sites of the adsorbent, which lead to higher adsorption. The lower percentage removal at higher dye concentration could be due to the saturation of the adsorptive sites of the adsorbent (Özer *et al.*, 2007).

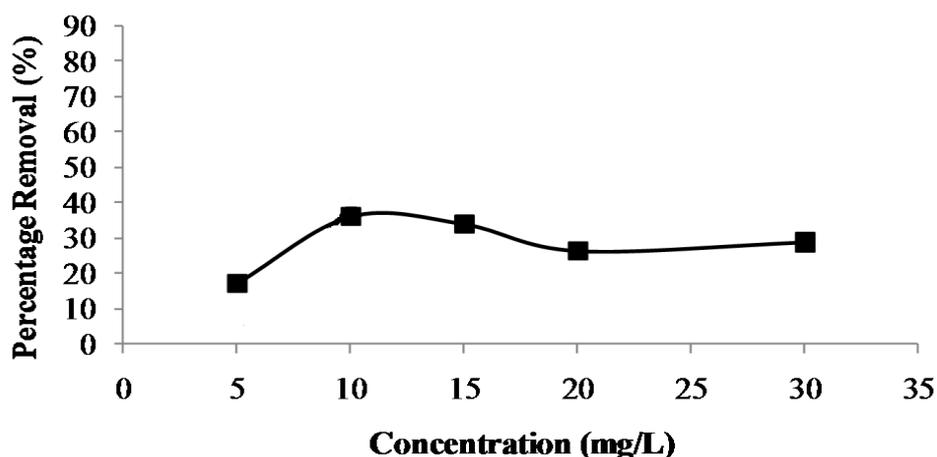


Fig. 8: Effect of Initial Concentration on Percentage Removal of MO by MCH

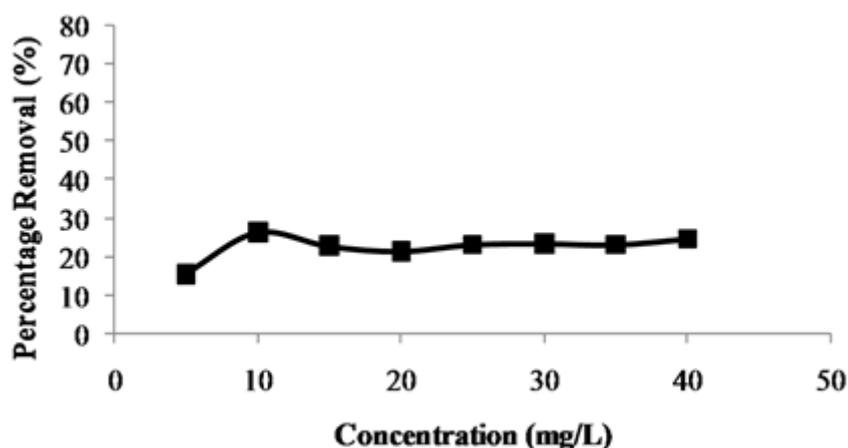


Fig. 9: Effect of initial concentration on the percentage removal of MO by RCH

ADSORPTION KINETICS

In order to study the adsorption kinetics of the selected dye on raw chitin (RCH) and modified chitin (MCH) adsorbents, two kinetic models: pseudo-first-order and pseudo-second-order models were selected to fit the kinetic data obtained from the adsorption of the selected azo dyes.

Pseudo-first-order Kinetic

The kinetics of MO adsorption onto chitin (RCH) and modified chitin (MCH) at different initial adsorbate concentrations with time were investigated by pseudo-first-order as reported by Tütem *et al.* (1998) and Ho and McKay (1998) from equation 3.

$$\log(q_e - qt) = \log q_e - \frac{k_1}{2.303} xt \quad (3)$$

where, q_e is the dye adsorbed onto unit mass of adsorbent (mg/g) and q_t is the adsorption capacity at time t of dye adsorbed (mg/L), k_1 is the adsorption rate constant (min^{-1}).

The linear plots of pseudo-first and second-order kinetic equations revealed the values of k_1 , k_2 , q_e and coefficients of determination (R^2) and were compared as shown in Tables 1 and 2 for chitin (RCH) and modified chitin (MCH) respectively. Although the coefficients of determination for the pseudo-first-order kinetic model obtained at room temperature were reasonable, the calculated q_e values do not agree with the experimental values. Hence, the pseudo-first-order kinetic model cannot satisfactorily be used to interpret the adsorption of MO by both RCH and MCH. As equally observed by Lin and Zhan (2012).

Table 1. Pseudo-first-order constants and coefficient of determinations of MO by RCH and MCH

Adsorbent	Conc. (Mg/L)	Pseudo-first-order Parameters			
		$q_{e, \text{exp}}$ (mg/g)	$q_{e, \text{cal}}$ (mg/g)	k_1	R^2
RCH	40	2.99	2.13	-0.088	0.758
MCH	40	7.04	3.89	-0.212	0.997

Pseudo-second-order kinetic

The linear form of pseudo-second-order kinetic model has been applied to various adsorption systems and the kinetic model is expressed by equation 4 (Ho and McKay 1998, Otero *et al.* 2003):

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 g/ (mg min) is the rate constant of the pseudo-second-order kinetic.

Pseudo-second-order model was also applied to interpret the adsorption of MO on both adsorbents. It was observed that the coefficients of

determination obtained from this model were higher than the ones obtained from pseudo-first-order model. It was also deduced from the results of this model that the calculated q_e values were close to the experimental q_e values. This indicate that the adsorption of the selected dye by both chitin (RCH) and modified chitin (MCH) were best described by the pseudo-second-order kinetic model. Similar phenomenon was also reported by other researchers (Nasuha *et al.*, 2011, Hameed and Ahmad, 2009). When t/q_e was plotted against t , the linear relationship graph was obtained, indicating the validity of the model in the adsorption of MO by RCH and MCH. The straight-line plots of t/q_e versus t were used to determine the k_2 , q_e , and R^2 values. The linear plots of t/q_e versus t were found

to be close to the experimental data with values of R^2 close to 1 as shown in Table 2. This indicates that the pseudo-second-order kinetics model can perfectly be used to interpret the sorption of MO on the RCH and MCH. This is similar to a study

reported by other researchers when they used chitin and chitosan to remove toluene from aqueous solution (Mohamed and Ouki, 2011).

Table 2. Pseudo-second-order constants and coefficient of determinations of MO by RCH and MCH

Adsorbent	Pseudo-second-order Parameters					
	Conc. (Mg/L)	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	K_2 ($g\ mg^{-1}\ min^{-1}$)	h ($g\ mg^{-1}\ min^{-1}$)	R^2
RCH	40	1.47	1.41	1.83	3.96	0.997
MCH	40	1.77	1.66	1.98	6.20	0.999

ADSORPTION ISOTHERM

Langmuir and Freundlich adsorption models were used to investigate and compare the adsorption capacities of RCH and MCH.

Langmuir Isotherm

This type of isotherm is widely used for the adsorption of pollutants from aqueous media. The adsorption capacity of the adsorbent is one of the most vital parameters in determining the efficiency of the adsorbent. The Langmuir isotherm model was used to obtain the maximum monolayer adsorption capacity of MO onto RCH and MCH. Hence, a plot of C_e/q_e against C_e should give a straight line graph as defined by equation 5 (Wen *et al.*, 2011):

$$\frac{C_e}{q_e} = \frac{1}{K \cdot Q_a} + \frac{C_e}{Q_a} \quad (5)$$

where K is the adsorption equilibrium constant (L/mg) which is related to the apparent energy of adsorption, Q_a is the quantity of the adsorbent required to produce a single monolayer or unit mass of the adsorbent (mg/g) and q_e is the amount of the adsorbate on the unit mass of the adsorbent (mg/g) when equilibrium concentration is C_e (mg/L). The isotherm plots of C_e/q_e versus C_e for the adsorption of MO onto RCH and MCH revealed the values of R^2 , K_L and Q_a as shown in Table 3.

The assumptions made by Langmuir isotherm is that, adsorption takes place at selected sites within the adsorbent (monolayer coverage), and there will be no further adsorption once the adsorbate occupies the selected sites of the adsorbent. The fundamental characteristic of Langmuir equation can be expressed in terms of dimensionless separation factor R_L , defined by equation 6.

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

where R_L is the Separation factor, K_L is the Langmuir constant, Q_a is the monolayer adsorption capacity and C_o is the concentration of the equilibrium aqueous phase of the adsorbate.

The values of $0 < R_L < 1$, $R_L > 1$, $R_L = 1$ and $R_L = 0$ indicate: favorable, unfavorable, linear and irreversible isotherms respectively (Mathlouthi and Roge 2003). The straight-lines plots of C_e/q_e against C_e were used to obtain K_L , Q_a and R^2 as shown in Table 3. The R_L values obtained for both RCH and MCH adsorbents (Table 3) indicate that the adsorption is favourable since both values are less than 1 ($0 < R_L < 1$).

Table 3. Langmuir isotherm constants and coefficients of determination on MO at 298K

Adsorbent	Adsorbate	Tem (K)	K_L (L/mg)	Q_a (mg/g)	R^2	R_L
RCH	MO	298	2.70	0.37	0.998	0.009
MCH	MO	298	1.15	0.87	0.999	0.021

Freundlich Isotherm

This type of model is not restricted to the formation of a monolayer, instead, it is applicable to adsorptions on heterogeneous surfaces involving the interaction between the adsorbed molecules. The equation for the Freundlich model according to Elizalde-González and Peláez-Cid, (2003) is represented by equation 7

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where q_e is the amount of adsorbate adsorbed at equilibrium per unit mass of the adsorbent (mg/g), K_F is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the adsorption intensity and C_e is the equilibrium concentration (mg/L). The $1/n$ and K_F values are obtained from the plot of $\log q_e$ against $\log C_e$ as slope and intercept respectively. The Freundlich isotherms plots for the adsorption of MO onto RCH and MCH were used to determine K_F and n values

which are the characteristic constants that reveal the nature of the adsorption as listed in Table 4. It is well known that the adsorption capacity of the adsorbent increase with increase in K_F . The values

of $1/n$ describe the adsorption intensity and indicate whether the isotherm is favorable ($0.1 < 1/n < 0.5$) or unfavorable ($1/n > 2$) (Zhang *et al.*, 2013).

Table 4. Freundlich isotherm constants and coefficient of determination for MO at 298K

Adsorbent	Adsorbate	Temp (K)	K_F (mg/g)	$1/n$	R^2
RCH	MO	298	16.87	1.032	0.995
MCH	MO	298	23.55	1.497	0.848

CONCLUSION

Chitin and modified chitin were used to remove methyl orange from aqueous solutions. The adsorption capacity of both chitin and modified chitin was found to increase with increase in solution pH, adsorbent dosage, contact time and initial dye concentration. The pseudo-second-order model fits the experimental data well as compare to pseudo-first-order kinetic, it is observed that the coefficients of determination obtained from Langmuir equations are higher than those obtained from Freundlich equations, since it offered R^2 values > 0.99 . This indicates that the Langmuir model could be adequately applied for comparative study, as it favors monolayer adsorption of MO onto the surfaces of RCH and MCH at given concentrations of the adsorbents and adsorbates.

REFERENCES

- Abu Naim, A., Umar, A., Sanagi, M. M. and Basaruddin, N. (2013). Chemical Modification of Chitin by Grafting with Polystyrene using Ammonium Persulfate Initiator. *Carbohydrate Polymers*, 98(2): 1618-1623.
- Akkaya, G., Uzun, İ. and Güzel, F. (2009). Adsorption of some Highly Toxic Dye-stuffs from Aqueous Solution by Chitin and its Synthesized Derivatives. *Desalination*, 249(3): 1115-1123.
- Aly, A.S., Jeon, B.D. and Park, Y.H. (1997). Preparation and Evaluation of the Chitin Derivatives for Wastewater Treatments. *Journal of Applied Polymer Science*, 65(10): 1939-1946.
- Bhatnagar, A. and Sillanpää, M. (2009). Applications of Chitin-and Chitosan-Derivatives for the Detoxification of Water and Wastewater – A Rhort review. *Advances in Colloid and Interface Science*, 152(1): 26-38.
- Bekçi, Z., Özveri, C., Seki, Y. and Yurdakoç, K. (2008). Sorption of malachite green on Chitosan Bead. *Journal of hazardous materials*, 154(1–3): 254-261.
- Bekçi, Z., Seki, Y. and Cavas, L. (2009). Removal of Malachite Green by using an Invasive Marine Alga *Caulerpa Racemosa* var. *Cylindracea*. *Journal of Hazardous Materials*, 161(2–3): 1454-1460.
- Dawood, S. and Sen, T.K. (2012). Removal of Anionic Dye Congo Red from Aqueous Solution by Raw Pine and Acid-Treated Pine Cone Powder as Adsorbent: Equilibrium, Thermodynamic, Kinetics, Mechanism and Process Design. *Water Research*, 46(6): 1933-1946.
- El-Latif, M.A., Ibrahim, A.M. and El-Kady, M. (2010). Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions using Biopolymer Oak Sawdust Composite. *Journal of American science*, 6(6): 267-283.
- Elizalde-González, M.P. and Peláez-Cid, A.A. (2003). Removal of Textile Dyes from Aqueous Solutions by Adsorption on Biodegradable Wastes. *Environmental Technology*, 24(7): 821-829.
- Ghaedi, M., Hassanzadeh, A. and Kokhdan, S.N. (2011). Multiwalled Carbon Nanotubes as Adsorbents for the Kinetic and Equilibrium Study of the Removal of Alizarin Red S and Morin. *Journal of Chemical & Engineering Data*, 56(5): 2511-2520.
- Giles, C.H. and Hassan, A.S.A. (1958). Adsorption at Organic Surfaces. V. A Study of the Adsorption of Dyes and other Organic Solutes by Cellulose and Chitin. *Journal of The Society of Dyers and Colourists*, 74: 846-857.
- Grełuk, M. and Hubicki, Z. (2009). Sorption of SPADNS Azo Dye on Polystyrene Anion Exchangers: Equilibrium and Kinetic Studies. *Journal of Hazardous Materials*, 172(1): 289-297.
- Hameed, B. and El-Khaiary, M. (2008). Batch Removal of Malachite Green from Aqueous Solutions by Adsorption on Oil Palm Trunk Fibre: Equilibrium Isotherms and Kinetic Studies. *Journal of Hazardous Materials*, 154(1): 237-244.
- Hameed, B. and Ahmad, A. (2009). Batch Adsorption of Methylene Blue from Aqueous Solution by Garlic Peel, an Agricultural Waste Biomass. *Journal of Hazardous Materials*, 164(2): 870-875.
- Ho, Y.S. and McKay, G. (1998). Sorption of Dye from Aqueous Solution by Peat. *Chemical Engineering Journal*, 70(2): 115-124.

- Hsu, S.-T., Lin, W.-C., Hsiao, W.-F., Lee, C.-C., Pan, T.-C., Wang, T.-T. and Huang, Y.-M. (2013). Preparation of Methacrylic Acid-Grafted Chitin using Cerium (IV) ion and its Application in Adsorbing Paraquat. *Journal of Applied Polymer Science*, 127(1): 760-764.
- Hsu, Y.C., Chiang, C.C. and Yu, M.F. (1997). Adsorption Behavior of Basic Dyes on Activated Clay. *Separation Science and Technology*, 32(15): 2513-2534.
- Huang, C.-M., Chen, L.-C., Yang, H.-C., Li, M.-H. and Pan, T.-C. (2012). Preparation of Acrylic Acid-Modified Chitin Improved by an Experimental Design and its Application in Absorbing Toxic Organic Compounds. *Journal of Hazardous Materials*, 241-242: 190-196.
- Khedr, S.A., Shouman, M.A. and Attia, A.A. (2013). Adsorption Studies on the Removal of Cationic Dye from Shrimp Shell using Chitin. *Biointerface Research in Applied Chemistry* 3(1).
- Lin, J. and Zhan, Y. (2012). Adsorption of Humic Acid from Aqueous Solution onto Unmodified and Surfactant-Modified Chitosan/Zeolite Composites. *Chemical Engineering Journal*, 200–202(0): 202-213.
- Longhinotti, E., Pozza, F., Furlan, L., Sanchez, M.D.N.D.M., Klug, M., Laranjeira, M.C.M. and Fávere, V.T. (1998). Adsorption of Anionic Dyes on the Biopolymer Chitin. *Journal of the Brazilian Chemical Society*, 9(5): 435-440.
- Lorenc-Grabowska, E. and Gryglewicz, G. (2005). Adsorption of Lignite-erived Humic Acids on Coal-based Mesoporous Activated Carbons. *Journal of Colloid and Interface Science*, 284(2): 416-423.
- Malik, R., Ramteke, D.S. and Wate, S.R. (2007). Adsorption of Malachite Green on Groundnut Shell Waste based Powdered Activated Carbon. *Waste Management* 27(9): 1129-1138.
- Mathlouthi, M. and Roge, B. (2003). Water Vapour Sorption Isotherms and the Caking of Food Powders. *Food Chem.*, 82(1): 61-71.
- Mckay, G., Blair, H. and Gardner, J. (1982). Adsorption of Dyes on Chitin. I. Equilibrium Studies. *Journal of Applied Polymer Science*, 27(8): 3043-3057.
- Mohamed, M. and Ouki, S. (2011), Removal Mechanisms of Toluene from Aqueous Solutions by Chitin and Chitosan. *Industrial & Engineering Chemistry Research*, 50(16): 9557-9563.
- Nasuha, N., Zurainan, H., Maarof, H., Zubir, N. and Amri, N. (2011). Effect of Cationic and Anionic Dye Adsorption from Aqueous Solution by using Chemically Modified Papaya Seed, pp. 50-54.
- Otero, M., Rozada, F., Calvo, L., Garcia, A. and Moran, A. (2003). Kinetic and Equilibrium Modelling of the Methylene Blue Removal from Solution by Adsorbent Materials Produced from Sewage Sludges. *Biochemical Engineering Journal*, 15(1): 59-68.
- Özer, D., Dursun, G. and Özer, A. (2007). Methylene Blue Adsorption from Aqueous Solution by Dehydrated Peanut Hull. *Journal of Hazardous Materials*, 144(1-2): 171179.
- Pan, X. and Zhang, D. (2009). Removal of Malachite Green from Water by Firmiana Simplex Wood Fiber. *Electronic Journal of Biotechnology*, 12(4): 9-10.
- Reddy, S., Sivaramakrishna, L. and Varada Reddy, A. (2012). The use of an Agricultural Waste Material, Jujuba Seeds for the Removal of Anionic Dye (Congo Red) from Aqueous Medium. *Journal of hazardous materials*, 203: 118-127.
- Sharma, Y., Uma, S. and Upadhyay, G. (2009). Adsorptive Removal of a Basic Dye from Water and Wastewater by Activated Carbon. *Journal of Applied Science in Environmental Sanitation*, 4: 21-24.
- Shirsath, D.S. and Shrivastava, V.S. (2012). Removal of Hazardous Dye Ponceau-S by using Chitin: an Organic Bioadsorbent. *African Journal of Environmental Science and Technology*, 6(2): 115-124.
- Sivakumar, P. and Palanisamy, P. (2009). Adsorptive Removal of Reactive and Direct Dyes using Non-conventional Adsorbent-column Studies. *Journal of Scientific and Industrial Research*, 68: 894-899.
- Tunali, S. and Akar, T. (2006). Zn(II) Biosorption Properties of Botrytis Cinerea Biomass. *Journal of hazardous materials*. 131(1-3), 137-145.
- Tütem, E., Apak, R. and Ünal, Ç.F. (1998). Adsorptive Removal of Chlorophenols from Water by Bituminous Shale. *Water Research*, 32(8): 2315-2324.
- Wen, Y., Tang, Z., Chen, Y. and Gu, Y. (2011). Adsorption of Cr (VI) from Aqueous Solutions using Chitosan-coated Fly Ash Composite as Biosorbent. *Chemical Engineering Journal*, 175: 110-116.
- Wojciechowski, K. and Wolska, A. (2005). Substantivity and Spatial Structure of Soluble Polycyclic Dyes for Dyeing Cellulose Fibres. *Dyes and pigments*, 65(2): 111-116.

Yao, Z., Wang, L. and Qi, J. (2009). Biosorption of Methylene Blue from Aqueous Solution using a Bioenergy Forest Waste: Xanthoceras Sorbifolia Seed Coat. *CLEAN– Soil, Air, Water*, 37(8): 642-648.

Zhang, J., Zhai, S., Li, S., Xiao, Z., Song, Y., An, Q. and Tian, G. (2013). Pb(II) Removal of Fe₃O₄@SiO₂-NH₂ Core-shell Nanomaterials Prepared via a Controllable Sol-Gel Process. *Chemical Engineering Journal*, 215-216: 461-471.

Zhang, X. and Bai, R. (2003). Mechanisms and Kinetics of Humic Acid Adsorption onto Chitosan-coated Granules. *Journal of Colloid and Interface Science*, 264(1): 30-38.