

REMOVAL OF ORANGE G FROM AQUEOUS SOLUTIONS BY POLYSTYRENE-MODIFIED CHITIN

Abdulganiyu Umar^{a,c}, Mohd Marsin Sanagi^{a,b*}, Ahmedy Abu Naim^a, Wan Nazihah Wan Ibrahim^a, Aemi Syazwani Abdul Keyon^a, Wan Aini Wan Ibrahim^{a,b}

^aDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^bCentre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^cDepartment of Chemistry, Faculty of Science, Northwest University, P.M.B 3220, Kano, Nigeria

Article history

Received

16 March 2017

Received in revised form

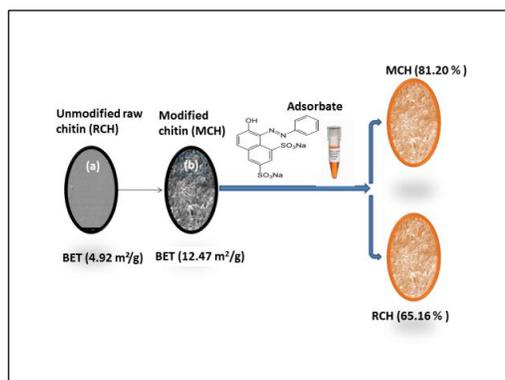
20 June 2017

Accepted

10 September 2017

*Corresponding author
marsin@kimia.fs.utm.my

Graphical abstract



Abstract

In this work, polystyrene modified-chitin was evaluated for the first time as adsorbent for the removal of Orange G from aqueous solutions. Its absorption capacity was compared to that of chitin. BET and FESEM results showed that the polystyrene-modified chitin has higher surface area (12.47 m²/g) compared to chitin (4.92 m²/g). Batch adsorption experiments on the removal of Orange G from aqueous solutions were conducted. The results showed that the polystyrene-modified chitin has improved adsorption capacity compared to chitin. The maximum adsorption of orange G by chitin occurred at pH 2, while that of the polystyrene-modified chitin occurred at pH 6. At an initial concentration of 20 mg/L, the percentages of dye removal were 65.16% and 81.20% for raw chitin (RCH) and polystyrene-modified chitin (MCH), respectively. Kinetics studies for the adsorbents were conducted using pseudo-first-order and pseudo-second-order models. The pseudo-first-order model gives poor fittings for both adsorbents, with low coefficients of determination (R²). The pseudo-second-order model fits the experimental data well, with R² close to unity. Langmuir and Freundlich models were used to interpret the adsorption isotherms. It was found that Langmuir isotherm conformed better than Freundlich model in the adsorption of selected dye on chitin and the polystyrene-modified chitin, with R² nearly unity.

Keywords: Chitin, grafting, polystyrene-modified chitin, orange G, adsorption

Abstrak

Dalam kajian ini, kitin terubahsuai polistirena telah dinilai buat pertama kali sebagai penyerap untuk penyingkiran jingga G daripada larutan akueus. Kapasiti penyerapannya telah dibandingkan dengan kapasiti penyerapan kitin. Keputusan BET dan FESEM menunjukkan bahawa kitin terubahsuai polistirena mempunyai luas permukaan yang meningkat (12.47 m²/g) berbanding kitin (4.92 m²/g). Eksperimen penyerapan pukal penyingkiran jingga G daripada larutan akueus telah dijalankan. Keputusan menunjukkan kitin terubahsuai polistirena mempunyai kapasiti penyerapan yang meningkat berbanding kitin. Penyerapan maksimum jingga G berlaku pada pH 2, manakala bagi kitin terubahsuai polistirena berlaku pada pH 6. Pada kepekatan awal 20 mg/L, peratus penyingkiran pewarna adalah masing-masing 65.16% dan 81.20% bagi kitin mentah (RCH) dan kitin terubahsuai polistirena (MCH). Kajian kinetic telah

dijalankan menggunakan model tertib-pertama-pseudo dan tertib-kedua-pseudo. Model tertib-pertama-pseudo menghasilkan data kurang memuaskan bagi kedua-dua penjerap, dengan pekali penentuan (R^2) yang rendah. Model tertib-kedua-pseudo pula sangat bersesuaian dengan data eksperimen, dengan R^2 menghampiri satu. Model Langmuir dan Freundlich telah digunakan untuk interpretasi isoterma penjerapan. Isotherma Langmuir didapati lebih mematuhi daripada model Freundlich dalam penjerapan pewarna terpilih pada kitin dan kitin terubahsuai polistirena, dengan R^2 menghampiri satu.

Kata kunci: Kitin, cangkukan, kitin terubahsuai polistirena, jingga G, penjerapan

© 2017 Penerbit UTM Press. All rights reserved

1.0 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 colored wastewaters even at low concentrations, resulting in water pollution [1]. The colored dye effluents are generally highly toxic to the aquatic biota, as they exhibit high color and high chemical and biochemical oxygen demands (COD and BOD) [2]. 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 [3]. Therefore, the removal of color from wastewater is even more important than the removal of the soluble colorless organic substances.

Azo dyes account for 60-70% of all dyes used commercially and they are the most problematic forms of dyes. This is because they do not undergo aerobic degradation but decomposed under anaerobic conditions to produce colorless aromatic amines that cause allergic reaction, dermatitis, skin irritation and are potentially carcinogenic [1, 3]. Therefore, increased interest has been focused on removing such dyes from the wastewater.

Different techniques have been used for the treatment of dye-bearing wastewater, such as chemical, physical and biological techniques, including biosorption, coagulation or flocculation, ozonation, advanced oxidation and membrane filtration [2, 4]. Adsorption is considered as the most effective techniques for the removal of dyes from wastewater due to its simplicity, ease of operation, cost effectiveness and its non-sensitivity to toxic substances [2, 4a]. Several materials have been used as adsorbents e.g. activated carbon, synthetic resins and silica, but their low cost-effectiveness and non-biodegradability limits their applications.

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 [5]. Adsorption of

anionic dyes namely orange IV, orange G and xylenol orange onto powdered chitin was reported [6]. Another research group used chitin to remove indigo carmine (IC) and tyrian blue (TB) dyes [7]. Chitin powder was used as bioadsorbent for the removal of ponceau-S dye from aqueous solution [8]. Polystyrene was used as ion-exchanger to remove azo dye 2-(4-sulphophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulphonic acid (SPADNS) from aqueous solution [9]. Acrylic acid and acrylonitrile-modified chitin was also used to remove C.I Acid Red106 and methylene blue dyes from aqueous solution [10]. The removal of selected acid and basic dyes using some chitin derivatives was reported [10]. Poly(acrylic) acid-modified chitin was used to remove some dyes in aqueous medium; indicating its potential in wastewater treatment [11]. Recently, methacrylic acid-modified chitin was used for the removal of paraquat from aqueous solution [12]. Chitin obtained from shrimp shells was also used as adsorbent for the removal of crystal violet dye from aqueous solution [13]. All previous literatures reported involved the use of either chitin or its modified form (using different vinyl monomers) or using polystyrene alone as adsorbent. However, no work has been reported on the use of prepared chitin-g-polystyrene copolymer as adsorbent for the removal of methyl (MO) orange and orange G dyes from aqueous solutions. Therefore, this work is aimed to compare the adsorption capacity of chitin to polystyrene-modified chitin by studying the influence of physicochemical parameters, such as pH, dye concentration and contact time on the removal of orange G. This study reveals vital information on the adsorption capacity (mg/L), adsorption mechanism and adsorption favorability of the prepared material.

2.0 METHODOLOGY

2.1 Materials and Methods

Chitin from crab shells, acetone, orange G (OG), chloroform and ethyl benzene were purchased from Sigma-Aldrich (St. Louis, USA). Styrene was purchased from Acros (New Jersey, USA). Ether (anhydrous) was purchased from J.T Baker (Centre Valley, U.S.A), and methanol from QR&C (Selangor, Malaysia). All

reagents and solvents were used directly as received without further purification, except styrene.

2.2 Characterization and Equipments

IR spectrum was recorded on a Perkin Elmer (Spectrum™ 400 Fourier transform infrared (FTIR) spectrometer, USA). The morphology of raw (unmodified) chitin (RCH) and modified chitin (MCH) were determined by Field emission scanning electron microscope (FESEM) analysis using a JEOL (JSM-7800F, Japan). UV-visible spectrophotometer (LAMBDA 35, Perkin Elmer) (Massachusetts, USA) was used to determine the dye (colour) concentrations in the aqueous media. The concentrations of the residual dyes (decolouration) were measured using UV-visible spectrophotometer at a λ_{\max} corresponding to the maximum adsorption for the dye solution ($\lambda_{\max} = 472.48$ nm OG)

BET analysis was employed to determine the physical characteristics of chitin and polystyrene-modified chitin, including specific surface area, pore diameter and pore volume, using a 2400 Series II CHND/O Analyzer (Perkin Elmer) at 77 K in liquid nitrogen. The pH of the chitin solution and dye concentrations were measured using a Denver pH 700 pH meter obtained from Cole Palmer (Illinois, USA).

2.3 Dissolution of Chitin

The soluble chitin was prepared according to the literature [14]. Dry chitin (1 g) was added to a 25mL flask containing 40% aqueous NaOH (15 mL) and transferred to a rotary vacuum evaporator for 3 h at 25 °C under reduced pressure. The chitin solution was then dissolved followed by vigorous stirring with 70 g of crushed ice below 0 °C. Concentrated aqueous HCl was added to the alkali chitin solution until the pH reached 12. The above alkaline solution was then neutralized to pH 7 by adding 0.1 M aqueous HCl drop-wise to obtain neutral solution. The solution was transferred into a 250mL 3-neck flask equipped with nitrogen inlet tube, condenser and magnetic stirrer, standing in an oil bath. The initiator was added to the chitin solution and stirred for 20 min as pre-interacting time. The monomer (styrene) was added and the reaction mixture was stirred at 60 °C and 3 h reaction time. The reaction was stopped by pouring the mixture into methanol. The precipitate was filtered using sintered funnel and the extract was dried in an oven to constant weight. The crude polymer was washed with ethylbenzene (Soxhlet extraction) to remove any polystyrene homopolymer. The graft copolymer was dried in oven as a true copolymer used for adsorption study.

2.4 Preparation of the Dye Solutions

Stock solutions were prepared by dissolving approximately 0.01 g of the dye in deionized water, and it was made up to 10 mL in 10 mL volumetric flask. Experimental solutions were prepared by transferring

an aliquot of the prepared solutions and diluting them with deionized water. The pH solutions of the required concentrations were adjusted by the addition of either 0.1 M aqueous HCl or 0.1 M aqueous NaOH solution. All glassware and sampling bottles were cleaned, rinsed with deionized water and dried in an oven at 60°C.

2.5 Batch Adsorption Study

Adsorption study was conducted using batch method, whereby a known amount of adsorbent was mixed with dye solution at a fixed time. For each adsorption study, 10 mL of the dye solution was added to a 50 mL flask containing a fixed amount of the adsorbent. The flask was covered with paraffin paper and then stirred using magnetic bar stirrer at room temperature (25 °C) for a specified time. The adsorbate was separated from the adsorbents by centrifugation at 4000 rpm for 20 min. Other experimental parameters, namely time and concentrations of the adsorbate and adsorbent dosage were also optimized.

The equations below were used to determine the amount of dye adsorbed by the adsorbents [15]:

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

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 concentration of dye (mg/L).

The amount of dye adsorbed onto the adsorbents at t , q_t (mg/g), were also calculated using the mass balance equation below [15]:

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

where q_t is the dye adsorbed onto unit weight of adsorbent (mg/g), C_i is the initial concentration of dye (mg/g) and C_e is the residual concentration of dye (mg/g) at a given time, t . M is the adsorbent dose (g) and V is the volume of solution (L).

Similar experiments were repeated by using MCH to compare the amount of adsorption, q_t (mg/g) and the percentage dye removal between chitin and polystyrene-modified chitin.

3.0 RESULTS AND DISCUSSION

3.1 FTIR Spectroscopy

To ascertain the presence of polystyrene peaks in the modified chitin, the FTIR spectra of the raw chitin (RCH) and the modified chitin (MCH) were conducted and compared. Figure 1 shows FTIR spectra of (a) RCH and (b) MCH. Spectrum (b) indicates 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 chitin and chitosan at 3600-3200

cm^{-1} (O-H and N-H stretching) and 1659 cm^{-1} due to C=O stretching.

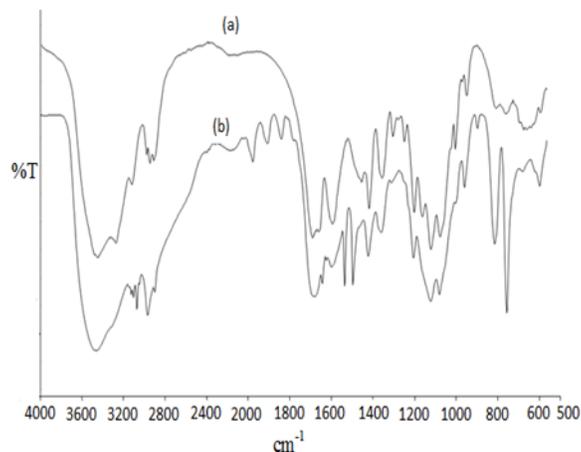


Figure 1 Infrared spectra of (a) RCH and (b) MCH.

Table 1 Physical properties of RCH and MCH*

Properties	RCH	MCH
BET surface area (m^2/g)	4.9183	12.4745
Langmuir surface area	10.5855	249.2589
Mesopore area (external surface area) (m^2/g)	4.9183	12.4745
Total pore volume V_t , (cm^3/g)	3.2774×10^{-2}	1.004×10^{-2}
Total mesopore volume V_m (cm^3/g)	3.2774×10^{-2}	1.004×10^{-2}
Average pore diameter (cm)	2.2225×10^{-6}	3.3246×10^{-7}

*RCH = raw chitin; MCH = modified chitin.

3.2 FESEM

From the FESEM images of CH (Figure 2a) and MCH (Figure 2b-d) it can be seen that the MCH possesses more porous sites than chitin. The increase in texture and porosity of the MCH could increase the adsorption capacity by trapping the dye molecules during the adsorption process. This phenomenon was also reported by Tunali & Akar [16].

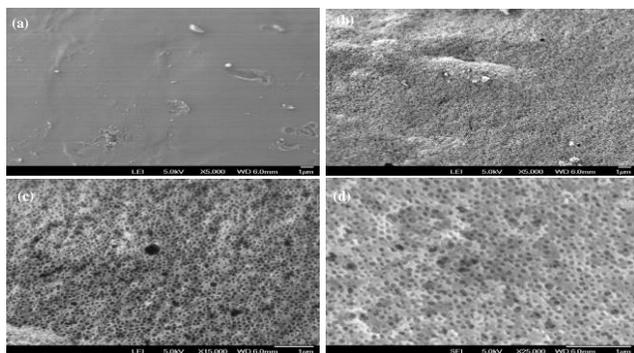


Figure 2 FESEM micrographs of (a) RCH and (b-d) MCH

3.3 BET (N_2) Adsorption

The physical characteristics of both RCH and MCH were studied and compared. The surface area was determined by the BET method [17], while the total pore volume and micropore volume were measured by the Barrett-Joyner-Halenda (BJH) [18] and the t-plot and Harkins-Jura methods, respectively [19]. The BET and Langmuir surface areas of the MCH were $12.4745 \text{ m}^2/\text{g}$ and $249.2589 \text{ m}^2/\text{g}$, respectively, with pore volume and size of $1.004 \times 10^{-2} \text{ cm}^3/\text{g}$ and $3.32462 \times 10^{-7} \text{ cm}$ (BET); and that of the unmodified RCH, having BET and Langmuir surface areas of $4.9183 \text{ m}^2/\text{g}$ and $10.5855 \text{ m}^2/\text{g}$ with pore volume and size of $0.032774 \text{ cm}^3/\text{g}$ and $2.2225 \times 10^{-6} \text{ cm}$ (BET) (Table 1). From the table, it can be deduced that MCH has improved physical characteristics (BET surface area) compared to RCH.

3.4 Effect of Solution pH on the Adsorption of Orange G

The effect of different pH of the solution on the adsorption of orange G by CH and MCH were investigated in the pH range of 1-7 (Figure 3). The results showed that the adsorption capacity of both the CH and MCH were pH dependent. Both polymers have OH and NH_2 functional groups. Since the studies were carried out in acidic and neutral media, it is

expected that in acidic media, both OH and NH₂ could be protonated. The hydroxyl groups in particular, could be heavily hydrated as such it would be basically unable to form hydrogen bonds with dye. Hence, the dye could be adsorbed via van der Waals interactions [20].

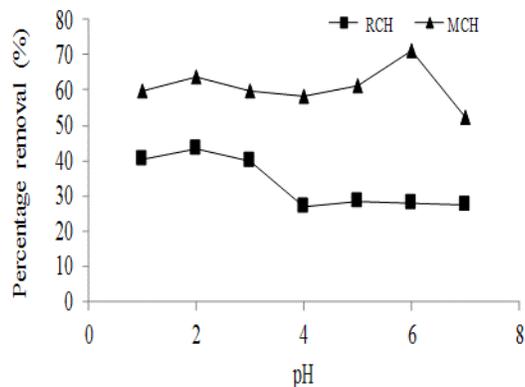


Figure 3 Effect of initial pH on the percentage removal of OG by raw chitin (RCH) and modified chitin (MCH) at 25 °C, 20 mg/L (10 mL) OG, contact time 50 min and 100 mg adsorbent

The percentage removal of orange G for MCH was found to be higher than that for CH. This could be attributable to the bulky nature of the OG, having three aromatic rings. It is believed that adsorption capacity depends not only on the number and type of functional groups or on the chemical and physical structures of the macroporous matrix, but also on the structure of organic compound [21]. As such, orange G molecules could be easily trapped by MCH. Also since the polystyrene side chains were attached to the backbone of the chitin, the porous nature of the polystyrene could also enhance the trapping of the dye molecules, thereby improving the percentage removal as compared to CH. Similar observations were reported by other researchers when styrene alone and styrene-divinylbenzene matrices were used as macroporous ion-exchange resins in the removal of azo dyes [9].

The percentage removal of OG by RCH was favored at lower pH value (pH 2) as shown in Figure 3. This could be due to limited number of amine (NH₂) functional groups associated with the chitin. It is well known that the intra-particle diffusion rate increase with decrease in pH. This could result in higher diffusivity of OG within the adsorbent pores at lower pH [15, 22].

In OG molecule, there are two sulphonic groups in their sodium salt form (SO₃Na), which dissociate in aqueous medium to yield two negatively charged end groups per dye molecule. Thus, the large amount of the negatively charged species in the solution could only be neutralized/adsorbed by highly positively charged RCH surfaces via electrostatic interaction, since it has less amine groups as adsorptive sites [6, 23].

3.5 Effect of Contact Time

The effect of contact time on the percentage removal of OG by RCH and MCH were studied using 20 mg/L (10 mL) of dye, 100 mg adsorbent dose and solutions pH 2 and 6 as shown in Figure 4. The percentage dye removal was found to increase with time. There was a rapid percentage dye removal in the beginning from 10 to 30 min, indicating the increase in the affinity of the adsorbates toward adsorbents by directing their functional groups (SO₃⁻) to the positively charged sites of the adsorbents. The adsorption continued slowly, until it reached equilibrium at 50 min with percentage removal of 28.95% and 64.71% OG for RCH and MCH, 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 unoccupied adsorptive sites in the adsorbent. The infinitesimal increase in the percentage dye removal could be due to the decrease in the number of available adsorptive sites in the adsorbents, until the sites are saturated [24].

3.6 Effect of Initial Dye Concentration

The percentage removal of the dye showed a decreasing trend with increasing dye concentrations as shown in Figure 5. It was observed that the percentage removal of OG adsorbed by both adsorbents increased from 5 to 20 mg/L, with maximum of percentage dye removals of 61.5% and 81.20%, respectively, and then decrease with increasing dye concentration. 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 [25].

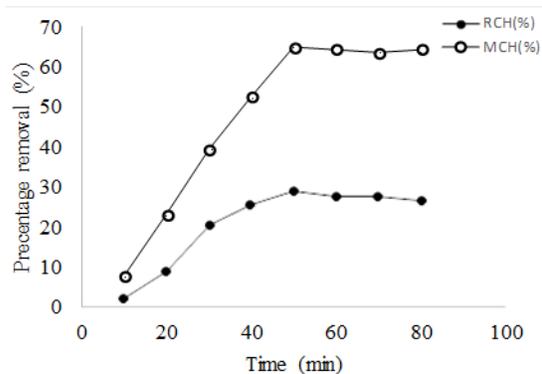


Figure 4 Effect of contact time on the percentage removal of OG by raw chitin (RCH) and modified chitin (MCH) at 25°C, 20 mg/L (10 mL) OG and 100 mg adsorbent

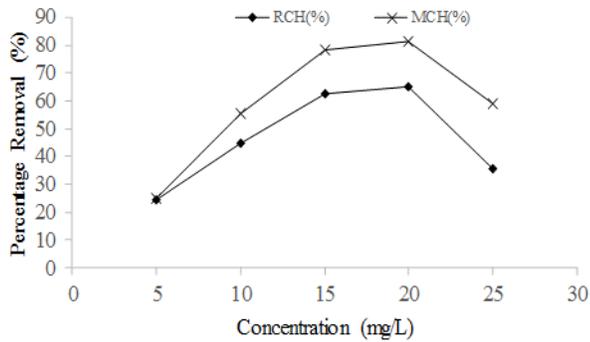


Figure 5 Effect of initial dye concentration on the percentage removal of OG by raw chitin (RCH) and modified chitin (MCH) at 25 °C, 20 mg/L (10 mL) OG, contact time 50 min and 100 mg adsorbent

3.7 Adsorption Kinetics

To study the adsorption kinetics of the selected dye on RCH and MCH adsorbents, two kinetic models: pseudo-first order and pseudo-second order models were used to fit the kinetic data obtained from the adsorption of the OG.

3.7.1 Pseudo-First-Order Kinetic

The kinetics of OG adsorption onto RCH and MCH at different initial adsorbate concentrations with time were investigated by pseudo-first-order equation as shown by equation below [26]:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303) t \quad (3)$$

where, q_e is the dye adsorbed onto unit mass of adsorbent (mg/g) and q_t is the initial concentrations at time t of dye adsorbed (mg/L), k_1 is the adsorption rate constant (min^{-1}). The linear plots of pseudo-first-order kinetic equation revealed the values of k_1 , q_e and coefficients of determination (R^2) and they were compared as shown in Table 2 for RCH and MCH. 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 OG by both RCH and MCH. This phenomenon was also observed by other research group when unmodified and surfactant-modified chitosan/zeolite composites were used to adsorb humic acid from aqueous solution [15].

Table 2 Pseudo-first order constants and coefficient of determination for OG adsorption by RCH and MCH

Adsorbent	Pseudo-first order model			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2
RCH	9.78	3.14	0.221	0.968
MCH	6.00	3.01	0.220	0.968

3.7.2 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 as described below [26b, 27]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

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 OG on both adsorbents. When t/q_e was plotted against t , the linear relationship graph was obtained, indicating the validity of the model in the adsorption of OG by RCH (Figure 6) and MCH (Figure 7). The straight-line plots of t/q_t versus t were used to determine the k_2 , q_e , and R^2 values. The linear plots of t/q_t versus t were found to be close to the experimental data with values of R^2 close to 1 as shown in Table 3. This indicates that the pseudo-second-order kinetics model can perfectly be used to interpret the adsorption of OG 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 [28].

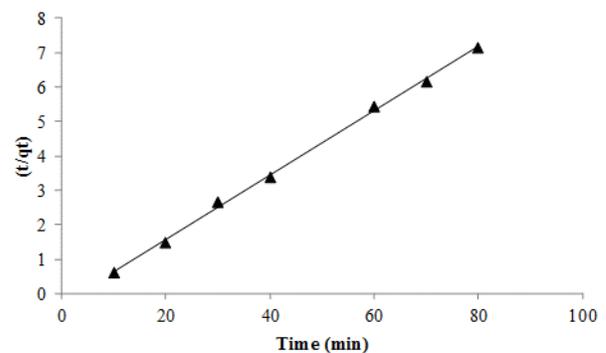


Figure 6 Pseudo-second-order kinetics plot of OG adsorption onto RCH at different concentrations, batch volume (10 mL) and 25 °C

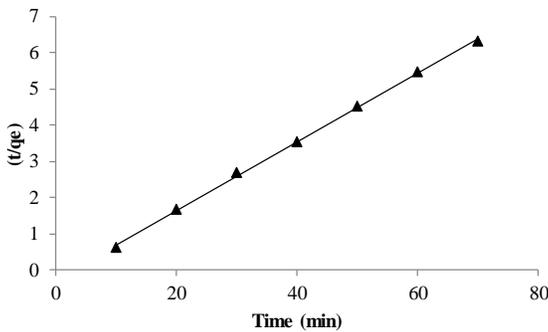


Figure 7 Pseudo-second-order kinetics plot for OG adsorption onto MCH at 25 °C; batch volume, 10 mL

Table 3 Pseudo-Second Order Constants and Coefficient of Determination for OG Adsorption by RCH and MCH

Adsorbent	Pseudo-second order model			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g/mg/ min)	R^2
RCH	2.11	2.14	1.40	0.998
MCH	2.11	2.11	1.10	0.999

3.8 Equilibrium Isotherms Studies

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

Table 4 Langmuir and Freundlich isotherms constants for OG adsorption by CH and MCH

Adsorbent	Langmuir model				Freundlich model		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)	$1/n$	R^2
CH	15.42	1.85	0.043	0.998	8.36	1.28	0.956
MCH	17.86	1.48	0.047	0.999	23.49	1.04	0.975

3.8.1 Langmuir Isotherm

The Langmuir isotherm model was valid for monolayer adsorption as expressed by the equation below [29]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \times q_{max}} \quad (5)$$

whereby the Langmuir adsorption constant (L/mg) which is related to the apparent energy of adsorption, q_{max} is the maximum quantity of the adsorbent required to produce a single monolayer or unit mass of the adsorbent and q_e is the amount of the adsorbate on the unit mass of the adsorbent (mg/g) at equilibrium and C_e is the equilibrium concentration (mg/L). The isotherm plots of C_e/q_e versus C_e for the adsorption of OG onto RCH and MCH revealed the values of R^2 and K_L as shown in Table 4.

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 [30]:

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

The R_L value reveals the nature of the isotherm: favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), respectively [18, 31]. The straight-

lines plots of C_e/q_e against C_e were used to obtain K_L and R^2 . The R_L values for RCH and MCH were calculated as 0.043 and 0.047 respectively, with coefficients of determination (R^2) 0.998 and 0.999 respectively. This indicates that the adsorption is favorable (Table 4).

3.8.2 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 is represented as [32]:

$$\log q_e = \log K_F + 1/n \log C \quad (7)$$

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. The Freundlich isotherms plots for the adsorption of OG 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.

4.0 CONCLUSION

Polystyrene -modified chitin (MCH) was used as adsorbent and its adsorption capacity was found to be higher than of unmodified chitin (RCH). The adsorption of orange G by both RCH and MCH were best described by the pseudo-second-order kinetic model as compared to the pseudo-first order kinetic model. The Langmuir model was also found to fit more than the Freundlich model in interpreting the adsorption capacities of both adsorbents. This indicates that the Langmuir model could be adequately applied for comparative study, as it favors monolayer adsorption of the selected dye by both RCH and MCH at given concentrations of the adsorbents and adsorbate.

Acknowledgement

The authors would like to thank Universiti Teknologi Malaysia and the Ministry of Education Malaysia for facilitations and postdoctoral fellowship for Abdulganiyu Umar and financial supports through research grants No. [Q. J130000.2509.09H84].

References

- [1] 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: 1933-1946.
- [2] 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: 642-648.
- [3] Bhatnagar, A., and Sillanpää, M. 2009. Applications of Chitin-and Chitosan-Derivatives for the Detoxification of Water and Wastewater—A Short Review. *Advances in Colloid and Interface Science*. 152: 26-38.
- [4] 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: 267-283.
- [5] 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: 2511-2520.
- [6] McKay, G., Blair, H., and Gardner, J. 1982. Adsorption of dyes on chitin. I. Equilibrium studies. *Journal of Applied Polymer Science*. 27: 3043-3057.
- [7] 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: 435-440.
- [8] Akkaya, G., Uzun, İ., and Güzel, F. 2009. Adsorption of Some Highly Toxic Dyes from Aqueous Solution by Chitin and Its Synthesized Derivatives. *Desalination*. 249: 1115-1123.
- [9] Shirsath, D. S., and Shrivastava, V. S. 2012. Removal of Hazardous Dye Ponceau-S by Using Chitin: An Organic Bioadsorbent. *Afr. J. Environmental Science Technology*. 6: 115-124.
- [10] Grelluk, M., and Hubicki, Z. 2009. Sorption of SPADNS Azo Dye on Polystyrene Anion Exchangers: Equilibrium and Kinetic Studies. *Journal of Hazardous Materials*. 172: 289-297.
- [11] 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: 1939-1946.
- [12] 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 Adsorbing Toxic Organic Compounds. *Journal of Hazardous Materials*. 241[242]: 190-196.
- [13] 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: 760-764.
- [14] 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.
- [15] Sannan, T., Kurita, K., and Iwakura, Y. 1975. Studies on Chitin, 1. Solubility Change by Alkaline Treatment and Film Casting. *Die Makromolekulare Chemie*. 176: 1191-1195.
- [16] 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: 1618-1623.
- [17] Lin, J., and Zhan, Y. 2012. Adsorption of Humic Acid from Aqueous Solution onto Unmodified and Surfactant-Modified Chitosan/Zelite Composites. *Chemical Engineering Journal*. 200 (202): 202-213.
- [18] Gregg, S. J., and Sing, K. S. W. 1982. *Adsorption, Surface Area and Porosity*. 2nd Ed. Academic Press.
- [19] Mathlouthi, M., and Roge, B. 2003. Water Vapour Sorption Isotherms and the Caking of Food Powders. *Food Chemistry*. 82: 61-71.
- [20] Barrett, E. P., Joyner, L. G., and Halenda, P. P. 1951. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* 73: 373-380.
- [21] 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. *J. Soc. Dyers Colour*. 74: 846-857.
- [22] Karcher, S., Kornmüller, A., and Jekel, M. 2001. Screening of Commercial Sorbents for the Removal of Reactive Dyes. *Dyes and Pigments*. 51: 111-125.
- [23] Lorenc-Grabowska, E., and Gryglewicz, G. 2005. Adsorption of Lignite-derived Humic Acids on Coal-based Mesoporous Activated Carbons. *Journal of Colloid and Interface Science*. 284: 416-423.
- [24] Zhang, X., and Bai, R. 2003. Mechanisms and Kinetics of Humic Acid Adsorption onto Chitosan-coated Granules. *Journal of Colloid and Interface Science*. 264: 30-38.
- [25] Wojciechowski, K., and Wolska, A. 2005. Substantivity and Spatial Structure of Soluble Polycyclic Dyes for Dyeing Cellulose Fibres. *Dyes and Pigments*. 65: 111-116.
- [26] 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: 870-875.
- [27] Özer, D., Dursun, G., and Özer, A. 2007. Methylene Blue Adsorption from Aqueous Solution by Dehydrated Peanut Hull. *Journal of Hazardous Materials*. 144: 171-179.
- [28] Tütem, E., Apak, R., and Ünal, C. F. 1998. Adsorptive Removal of Chlorophenols from Water by Bituminous Shale. *Water Research*. 32: 2315-2324.
- [29] Ho, Y. S., and McKay, G. 1998. Sorption of Dye from Aqueous Solution by Peat. *Chemical Engineering Journal*. 70: 115-124.
- [30] 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: 59-68.
- [31] Mohamed, M., and Ouki, S. 2011. Removal Mechanisms of Toluene from Aqueous Solutions by Chitin and Chitosan. *Industrial & Engineering Chemistry Research*. 50: 9557-9563.
- [32] 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.