FEB - FRESENIUS ENVIRONMENTAL BULLETIN
Founded jointly by F. Korte and F. Coulston
Production by PSP - Vimy Str. 1e, 85354 Freising, Germany in
cooperation with PRT-Parlar Research & Technology
Vimy Str 1e, 85354 Freising

Printed in Germany-ISSN 1018-4619

Fresenius Environmental Bulletin is abstracted/indexed in:
Biology & Environmental Sciences, BIOSIS, CAB International, Cambridge Scientific abstracts, Chemical Abstracts, Current Awareness, Current Contents/Agriculture, CSA Civil Engineering Abstracts, CSA Mechanical & Transportation Engineering, IBIDS database, Information Ventures, NISC, Research Alert, Science Citation Index (SCI), Scisearch, Selected Water Resources Abstracts

CONTENTS

ORIGINAL PAPERS

© by PSP Volume 27 – No. 5A/2018 pages 3386-3398 Fresenius Environmental Bulletin

LALA CLAM (*ORBICULARIA ORBICULATA*) SHELL AS AN ADSORBENT FOR ANIONIC AND CATIONIC DYES FROM AQUEOUS SOLUTION

Azlan Kamari[1,*], Arwa Alseddig Ahmed Eljiedi[1], Endang W Laksono[2], Norlaili Abu Bakar[1]

[1]Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900, Tanjong Malim, Perak, Malaysia
[2]Department of Chemistry Education, Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta, Kampus Karangmalang, Jl. Colombo No. 1, Yogyakarta 55281, Indonesia

ABSTRACT

In this work, lala clam shell was utilised as an alternative low-cost adsorbent for the remediation of water contaminated by two classes of dyes, namely anionic (Congo red (CR) and Methyl orange (MO)) and cationic (Methylene blue (MB) and Rhodamine B (RB)) dyes from aqueous solution. Batch adsorption experiments were performed to assess the effects of various experimental parameters such as solution pH, adsorbent dosage and initial adsorbate concentration. The applicability of lala clam shell to remove dyes from aqueous solution was evaluated in both single- and mix-systems. The optimum pH for CR, MO and RB removal was found at pH 2.0, while pH 8.0 was the optimum value for MB adsorption. At an initial concentration of 2.5 to 100 mg/L, the amount of four dyes adsorbed onto lala clam shell was in the order of CR> MB> RB> MO, in a single-dye adsorption system. Whereas, in the case of a mix-dye adsorption system, the amount of four dyes adsorbed was found in the order MB> RB> MO> CR. The adsorption equilibrium data were correlated with both Langmuir and Freundlich isotherm models. The results showed that the equilibrium data were perfectly represented by the Freundlich isotherm model. The biomass adsorbent was characterised using the Field Emission Scanning Electron Microscope (FESEM) and Fourier Transform Infrared (FTIR) Spectrometer. Overall, outcomes from this study suggested that lala clam shell, a fishery waste, can be beneficial and efficient instead of expensive adsorbents for water treatment.

KEYWORDS:
Adsorption, lala clam shell, dyes, water treatment

INTRODUCTION

Water contamination by various pollutants such as dyes, heavy metals and pesticides poses a serious threat to the environment and human health. Both organic and inorganic substances with a non-biodegradable characteristic can be accumulated in the environment. Water contamination causes around five million of the world population to die every year [1, 2]. Many industrial activities particularly plastic, textile, printing, transportation, food and leather [3, 4] have significantly contributed to water contamination. As a matter of fact, about 15% of dye contaminations are derived from textile and other industries, worldwide [5, 6]. For example, it was estimated that about 950 million tonnes of dyeing wastewater were produced in China in 2012 [7]. Hence, the treatment of water from these polluted environments is important for the ecological protection [8].

Dyes are classified based on their nuclear structure, namely as anionic and cationic. Anionic dyes have a negative charge due to the presence of sulphonate groups, meanwhile cationic dyes have a positive charge due the presence of protonated amine or sulphur groups in the aqueous solution. Industrial effluents containing both anionic and cationic dyes are of great concern. The anionic dyes (Congo red and Methyl orange) and cationic dyes (Methylene blue and Rhodamine B) are toxic and even carcinogenic [9]. Toxic dyes are normally presence in water environment at high concentrations. Due to their thermal stability as well as ability to absorb and reflect sunlight that enters the water, the photosynthesis of algae and aquatic plants will be reduced. This scenario will seriously affect the food chain. Furthermore, the presence of little amount of dyes in water can be highly visible and undesirable, making it unsafe for the human consumption [10]. For example, excessive levels of Methylene blue may cause a number of diseases such as digestive and respiratory systems problems, as well as nausea, vomiting and profuse sweating [11].

Chemical precipitation, coagulation-flocculation, electrochemical treatment and adsorption have been employed to sequester dyes from aqueous solution [12, 13]. Adsorption is one of the most effective treatment processes as it is a simple operation and incurs low operational cost as compared to other techniques; which have drawbacks like sludge formation, high energy and conservation cost. Undoubtedly, activated carbon is a popular and widely used adsorbent for organic dyes removal. This is

mainly due to its large surface area and high adsorption capacity. However, its application in developing countries is limited due to its high-cost production and regeneration issue [14, 15]. In 2013, the global market for activated carbon totalled $1.9 billion, driven primarily by Asia-Pacific and North American regions for application in water treatment and then reached $2.1 billion, in 2014 [16].

Effective adsorbents for water treatment should have several characteristics such as low-cost, readily available in large quantities and easily can be disposed. The capability of several low-cost and eco-friendly adsorbents such as *Luffa cylindrica* biomass [8], *Metroxylon* spp. waste [17], rice straw [11], orange peel [18], mesoporous hollow shells [5] and *Raphia hookerie* epicarp [3] to treat dye contaminated water has been assessed in the last few years. The key property was the presence of functional groups (hydroxyl, amine and carbonate) and lignocellulosic compounds in these adsorbents that contributed to bind dyes during the adsorption process.

In the present work, the natural waste from fishery industry, namely the short neck clam (*Orbicularia orbiculata*) shell or locally known as lala was used as an alternative adsorbent for water treatment. Lala clam shell is abundantly available in Malaysia, Indonesia and Libya with no economic value. It has not been used for purification of water contaminated by dyes. Moreover, the shell waste is primarily composed of calcium carbonate (95%), which may be beneficial for the adsorption mechanism [19]. Hence, the main objective of this study was to investigate the effectiveness of lala clam shell as an adsorbent for the removal of anionic and cationic dyes from aqueous solution in the single- and mix-dye systems. A systematic evaluation involving several experimental parameters such as the pH solution, initial adsorbate concentration and adsorbent dosage was performed.

MATERIALS AND METHODS

Chemicals. Lala clam shells were collected from a restaurant in Tanjong Malim, Perak. NaOH and HCl were purchased from HmbG Reagent Chemicals. In this work, two anionic (CR and MO) and two cationic (MB and RB) dyes were studied. The chemical structure and physiochemical properties of dyes studied are listed in Table 1. CR, MB and RB were supplied by Merck, while MO was acquired from Bendosen. All chemicals used were of analytical grade and deionised water was used throughout this study.

Preparation of adsorbent and adsorbate. The lala clam shells were washed and rinsed by using tap water, then thoroughly with deionised water to remove dirt. Finally, the shells were dried in an oven at 70 ^{o}C for 24 h. After drying, the shells were crushed and sieved through 150-250 µm size fractions by using a protocol of the American Society for Testing and Materials (ASTM) standard sieve. The stock solutions of 100 mg/L were prepared with appropriate amount of dyes (CR, MO, MB and RB) by dissolving in the deionised water. Each dye was prepared separately by dissolving 25 mg of the dye in 250 mL deionised water and then, the stock solution was diluted to the required concentrations.

Characterisation studies. The surface area and average pore diameter analyses were performed using a Quantachrome Autosorb 1 Surface Analyser. The Brunauer-Emmett-Teller (BET) multipoint technique [20] was applied for surface area measurement, while the Barrett, Joyner and Halenda method [21] was used for pore diameter determination.

The presence of functional groups on materials, as well as the interaction between functional groups with dyes were identified and studied using a Thermo Nicolet 6700 Fourier Transform Infrared (FTIR) Spectrometer. FTIR analysis was conducted over 32 cumulative scans in the wavenumber ranging from 4000 to 400 cm^{-1}. The surface morphology of the Lala clam shells before and after dye adsorption was examined using a Hitachi SU 8020 UHR Field Emission Scanning Electron Microscope (FESEM).

Adsorption experiments. The batch adsorption experiments were carried out in 250 mL conical flasks by adding approximately 0.5 g of an adsorbent in 50 mL of dye solution of the desired concentration at optimum conditions. The samples were equilibrated by shaking at 100 rpm for 1 h using a Protech Orbital Shaker (model 720) and samples were separated through a piece of filter paper (Filtre Fioroni 601, 110 mm). The concentration of dyes was measured using an Agilent Cary 60 UV-Vis spectrophotometer at maximum wavelength (λ_{max}) values as shown in Table 1. The calibration curve was lined between the absorbance and various concentration of the dye solution (1, 2, 3, 4 and 5 mg/L) to acquire the absorbance-concentration profile (equilibrium dye concentration).

The effect of pH solution was studied in the pH range of 2.0-8.0. The pH solution was adjusted by adding a few drops of diluted 0.05 mol/L HCl or 0.05 mol/L NaOH solutions, and measured using a pH meter. About 0.5 g of the adsorbent was added to 50 mL of 5 mg/L dye solution. The mixture was then shaken for 1 h at 100 rpm. The isotherm studies were accomplished by shaking 0.5 g of adsorbent in 50 mL of dye solution with an initial dye concentration ranging from 2.5 mg/L to 100 mg/L. The experiment was performed at an optimum pH. The effect of adsorbent dosage on adsorption capacity was studied using four various doses of adsorbent, ranging from 0.025 g to 0.200 g. The adsorbent was added into 50

mL of 5 mg/L dye solution, shaken and filtered as described earlier.

The competitive adsorption study was accomplished in the mix-dye system. About 0.5 g of lala clam shells was added to 50 mL solution containing (5, 20 or 100 mg/L) of each dye. The adsorption of the mix-dye system was investigated using a similar procedure to that of the single-dye system experiment. The equilibrium concentration of each dye was measured using the UV-Vis spectrophotometer. The dried filtrate was characterised using FTIR and FESEM.

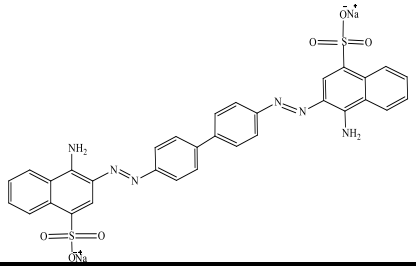
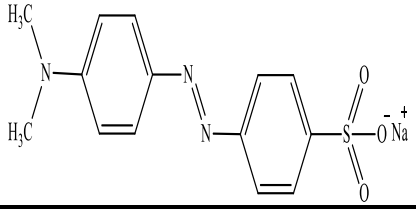
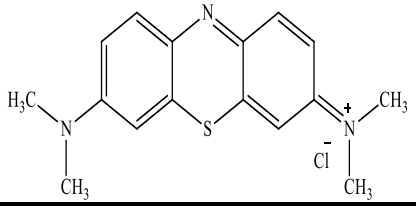
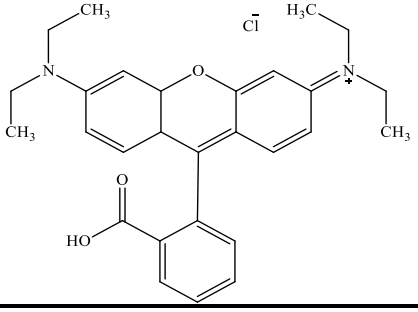
All experiments were run in triplicates. The adsorption capacity at equilibrium (q) was calculated using Equation (1):

$$q = \frac{(C_o - C_e)}{W} V \quad (1)$$

where q is the amount of dye adsorbed at equilibrium (mg/g), C_o is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), W is the weight of the adsorbent (g) and V is the volume of dye solution (L). The removal percentage of dye for the adsorption process was estimated using Equation (2):

$$\text{Removal \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

TABLE 1
The chemical structure and physiochemical properties of dyes studied.

Dyes	Chemical structures	Molecular weight (g/mol)	λ_{max} (nm)	Industrial use
Congo Red (CR)		696.67	499	Textiles, paper and rubber.
Methyl Orange (MO)		327.34	461	Printing and research laboratories.
Methylene Blue (MB)		319.85	665	Wood, silk and cotton.
Rhodamine B (RB)		479.02	554	Textiles, paper and leathers.

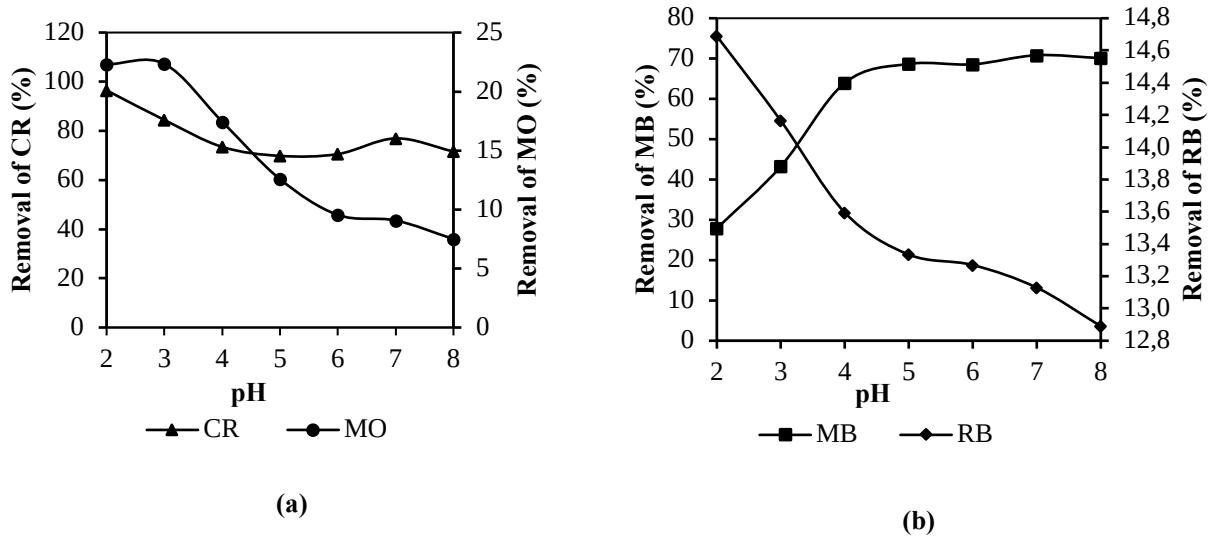


FIGURE 1
Effect of solution pH on adsorption of anionic dyes (a) and cationic dyes (b) onto lala clam shell.

RESULTS AND DISCUSSION

Adsorption studies. Single-dye system. Effect of solution pH. The expulsion of dyes from wastewater by adsorption is highly reliant on the pH of the solution, which influences the surface charge of the adsorbent, degree of ionisation and speciation of the adsorbate [22].

Figures 1(a) and 1(b) show the effect of pH solution on the percentage removal of anionic and cationic dyes by lala clam shells, respectively. It was clear that the percentage removal of two anionic dyes (CR and MO) decreased with an increase in the pH and optimum pH was recorded at pH 2.0 (Figure 1(a)). A similar optimum pH value was observed for adsorption of CR onto biomass of *Trametes pubescens* [23], adsorption of MO onto chitosan [24] and activated carbon [25]. This observation can be related to electrostatic repulsion between the sulfonates (SO_3^{2-}) groups and excessive OH^- ions at the high pH values.

In contrast, the effect of pH solution on the percentage removal of two cationic dyes (MB and RB) by lala clam shells is shown in Figure 1(b). The percentage removal of MB increased with an increase in the pH and the maximum removal efficiency was achieved at pH 8.0. In this case, the percentage removal of RB was decreased with an increase in the pH and the maximum efficiency was obtained at pH 2.0. A similar trend was reported for adsorption of MB by tea waste [26], *Imperata cylindrical* biomass [27] and adsorption of RB by steel slag [28]. The adsorption behaviour of MB and RB was greatly influenced by their functional groups.

MB, like other cationic dyes produced an intense molecular cation (C^+) and reduced ions (CH^+), which exists in aqueous solution in the form of positively charged ions [29, 30]. Thereby, the high pH values will cause the adsorbent surface become negatively charged and results in higher adsorption. Meanwhile, RB contains a carboxyl group structure as shown in Table 1. The sharp decreased in percentage removal at the higher pH values was likely due to electrostatic repulsion between the carboxyl group and the excessive hydroxide ions.

Effect of adsorbent dosage. The adsorbent dosage is one of the important parameters in determining the capacity of adsorbent and fundamental to optimise an adsorption system as adsorbent dosage controls the availability of adsorption site [31, 32]. Figure 2 presents the effect of adsorbent dosage on adsorption of CR, MB, RB and MO onto lala clam shells. It was observed that as the amount of adsorbent was increased, a sharp decrease in adsorption capacity from 9.8 mg/g to 1.5 mg/g, 7.5 mg/g to 0.8 mg/g, 1.5 mg/g to 0.2 mg/g and 2.5 mg/g to 0.1 mg/g was obtained for CR, MB, RB and MO, respectively.

A lower adsorbent dosage which presumed a larger overall total surface area of lala clam shell was being exposed and thus more dyes were adsorbed onto the surface per gram unit of lala. Besides, the higher adsorbent dosage surface of lala clam shell became masked due to the accumulation particles on the adsorbent; it thus created adsorbent aggregation and reduction in the total surface area of contact by the active sites, namely carbonate group (CO_3^{2-}) of lala clam shell. The same behaviour of other adsorbents on dyes was reported in the literature [22, 33, 34, 35].

Effect of initial adsorbate concentration. Experiments were carried out at different initial concentrations (2.5 to 100 mg/L) of dye, while the other parameters were kept constant and performed at optimum pH. Figure 3, presents the amount of dye ad-

sorbed as a function of initial concentration. It is essential to note that the amount of all dyes adsorbed by lala clam shells increased with an increase in the initial concentration of the dye solution. This outcome can be explained by two main factors, namely: (1) the probability of the increase due to the collision between the molecules of dyes and adsorbent surface, and (2) the high diffusion rate of dyes into adsorbent [36].

The amount of four dyes adsorbed onto lala clam shells was in the order of CR > MB > RB > MO. Although CR is an anionic dye, it contains two amine groups ($-NH_2$) and diazo groups (-N=N-) that can be potential protonation sites, and thus there are different possible types of protonated dye molecules [37]. Figure 4 shows the protonated CR at optimum pH [37, 38].

From Figure 4, in the acidic condition at optimum pH 2.0, it can be imagined that the protonated amino (NH_3^+) or azo nitrogens ($-N=NH^+$) having positive charge can be adsorbed over the high negatively charged CO_3^{2-} surface of lala clam shells. However, MO is also an anionic dye but contains one azo group (-N=N-), so it comes last in the order after two cationic dyes that can be adsorbed more than MO onto the surface of lala clam shells.

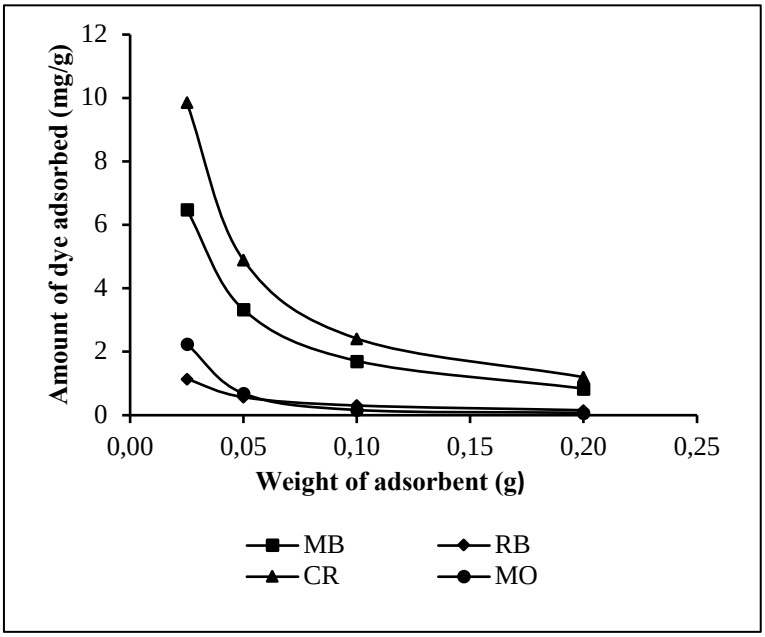


FIGURE 2
Effect of adsorbent dosage on adsorption of MB, RB, CR and MO.

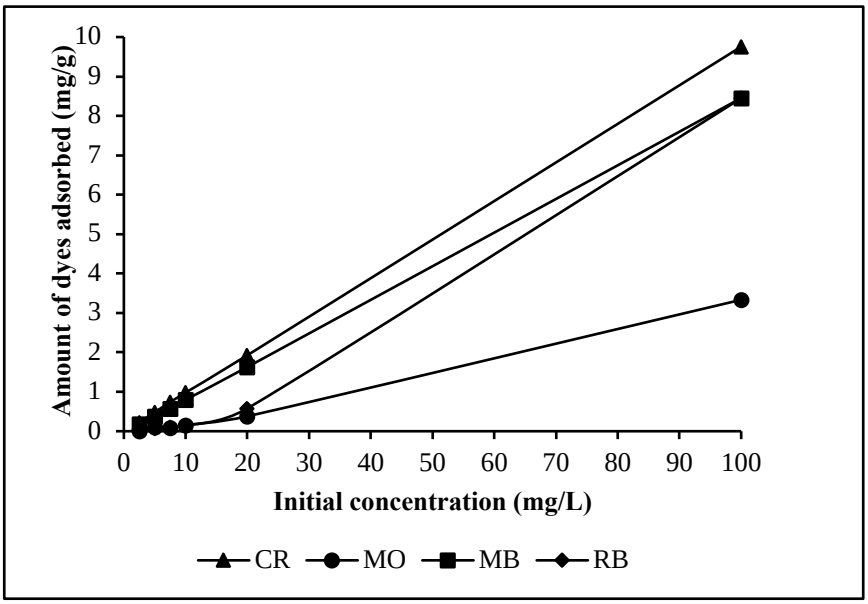


FIGURE 3
Effect of initial concentration on adsorption of MB, RB, CR and MO.

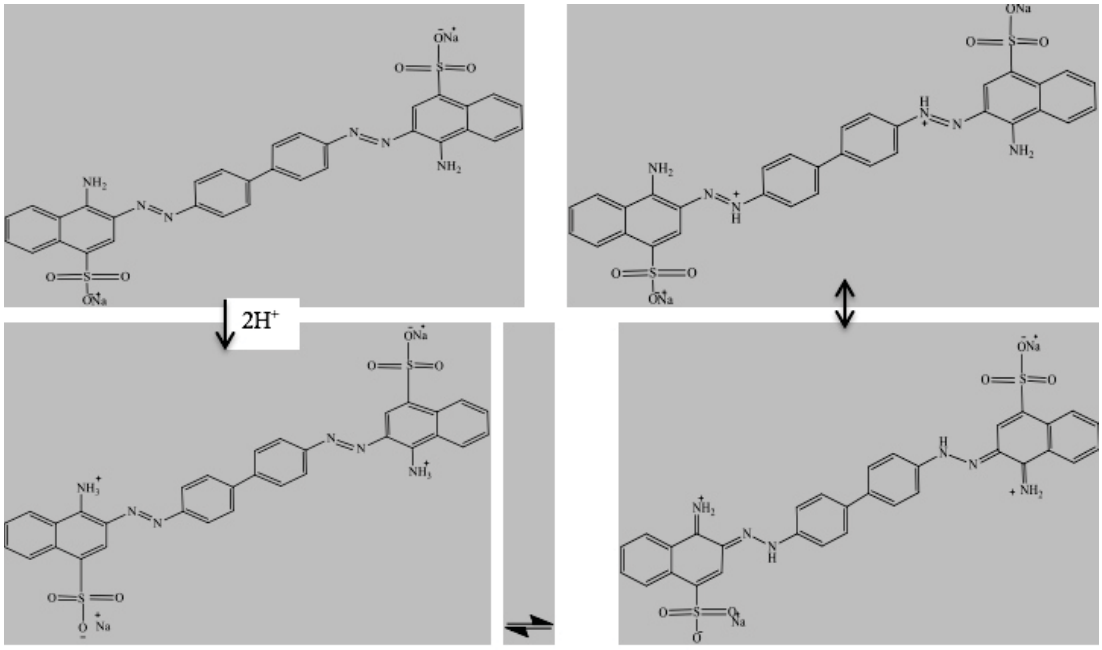


FIGURE 4
Protonated of CR at optimum pH 2.0. Adapted from [37, 38].

TABLE 2
Freundlich and Langmuir isotherm constants for adsorption of CR, MO, MB and RB onto lala clam shells.

Dyes	Freundlich			Langmuir		
	K_F (mg/g)	1/n	R^2	Q_{max} (mg/g)	b (L/mg)	R^2
CR	4.375	0.726	0.962	15.480	0.559	0.739
MO	0.010	0.677	0.959	1.004	0.013	0.286
MB	0.320	0.825	0.998	11.669	0.028	0.609
RB	0.014	0.496	0.699	0.311	0.047	0.641

Adsorption isotherms. The interaction and distribution of dyes on the surface of adsorbent are described using the adsorption isotherm models [36, 14]. Two widely used isotherm models, namely Freundlich and Langmuir were applied to analyse equilibrium data. Freundlich isotherm model is an empirical equation used to describe adsorption at multilayer heterogeneous with sites that had different energies of adsorption [14]. The linear form of the Freundlich equation is expressed as Equation (3) [39].

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (3)$$

where C_e is the equilibrium concentration of solute (mg/L), q_e the amount of solute adsorbed per unit weight of adsorbed at equilibrium (mg/g), K_F (mg/g) and n are the Freundlich constants related to adsorption capacity and intensity, respectively. The liner plot of log q_e against log C_e will give the K_F and n values.

The Langmuir isotherm model deals with adsorption at monolayer homogeneous surface of the adsorbent where all sites on adsorbents have equal energy [36]. The linear form of the Langmuir isotherm is represented by Equation (4) [40].

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \quad (4)$$

where Q is the maximum adsorption at monolayer (mg/g) and b is the Langmuir constant related to the affinity of binding sites (mL/mg). In addition, b is a measure of the energy of adsorption. The Q and b can be determined from the linear plot of C_e/q_e against C_e.

The isotherm constants and correlation coefficient (R^2) obtained from Freundlich and Langmuir isotherm models are listed in Table 2. Based on R^2 values, the equilibrium adsorption data for all dyes fitted the Freundlich isotherm model better than Langmuir isotherm, indicating the heterogeneous of the adsorbent surface. Similar results were obtained by Dey et al. [36] for MB removal using *Rhizopus oryzae* waste, Mahmoud et al. [18] for CR and MO adsorption using orange peel, and Balasubramani and Sivarajasekar [41] for RB removal using activated carbon. The 1/n values calculated from the Freundlich isotherm model lie between 0 and 1. This implies that the adsorption of four dyes onto Lala clam shells was favourable [42].

The adsorption capacities K_F calculated from the Freundlich isotherm equation for CR, MO, MB and RB, were 4.375, 0.010, 0.320 and 0.010 mg/g,

respectively. The removal of dyes by using several other adsorbents has been studied in the recent years and some of these reports provided K_F values. Although these values were obtained under different experimental conditions, they were useful to compare the performance and capacity of the adsorbents. The K_F value obtained in this study was greater than those reported for kaolin (1.089 mg/g for CR) [43], amine-functionalized hollow mesoporous shells (1.291 mg/g for CR) [5], *Rhizopus oryzae* (0.021 mg/g for MB) [36], sugarcane bagasse (0.110 mg/g for MB) [31] and activated geopolymer (0.002 mg/g for MO) [44].

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor (R_L), which is defined in the following Equation (5) [42]:

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

where C_o is the initial adsorbate concentration (mg/L), R_L is the value shows the nature of the adsorption process to be unfavourable (R_L>1), linear (R_L = 1), favourable (0<R_L<1), or irreversible (R_L = 0). The R_L values were 0.187, 0.825, 0.718 and 0.634 for CR, MO, MB and RB, following the adsorption by lala clam shells. It is clear that the R_L values were in the range of $0 < R_L < 1$. This suggests that the adsorption of four dyes was favourable.

The maximum adsorption capacity Q (mg/g) of lala clam shells for CR, MO, MB and RB were 15.48, 1.00, 11.66 and 0.31 mg/g, respectively. It was compared to other adsorbents. The maximum adsorption capacities of lala clam shells were compared to several other adsorbents, as shown in Table 3. The difference in Q values of the adsorbents can be related to their unique physical and chemical characteristics [54] and experimental conditions.

TABLE 3
The maximum adsorption capacities (Q_{max}) of several adsorbents.

Adsorbents	Dye	Q_{max} (mg/g)	References
Eichhornia crassipes root	CR	1.58	[45]
Peanut shell	CR	15.09	[46]
Zeolite	CR	3.77	[47]
Calcareous soil	MB	1.76	[33]
Cow dung ash	MB	5.31	[48]
Luffa cylindrical	MB	4.94	[8]
Rhizopus oryzae biomass	MB	8.20	[36]
Rice husk ash	MB	6.90	[49]
Spent rice biomass	MB	8.30	[50]
Activated carbon modified by silver nanoparticles	MO	0.69	[51]
Fly ash	MO	1.20	[52]
Humicola fuscoatra biomass	MO	0.50	[53]

TABLE 4
The amount of dye adsorbed onto lala clam shells in single- and mix-dye system.

Adsorption system	Dyes	Dye concentration (mg/L)		Amount of dye adsorbed (mg/g)
		Initial	Equilibrium	
Single-dye system	MB	5	0.57	0.44
		20	3.64	1.64
		100	4.32	9.56
	RB	5	3.00	0.22
		20	10.55	0.95
		100	13.01	8.73
	MO	5	3.99	0.10
		20	15.06	0.49
		100	57.30	4.28
	CR	5	0.10	0.48
		20	0.32	1.96
		100	1.59	9.84
Mix-dye system	MB	5	0.67	0.43
		20	1.51	1.84
		100	2.02	9.78
	RB	5	2.86	0.21
		20	10.32	0.96
		100	12.33	8.75
	MO	5	4.21	0.07
		20	14.31	0.56
		100	57.23	4.27
	CR	5	4.72	0.02
		20	18.95	0.10
		100	59.13	4.08

TABLE 5
Comparison of amount of dyes adsorbed onto lala clam shell and activated carbon in mix-dye system.

Adsorbent	Dyes	Dyes concentration (mg/L)		Adsorbent of dyes (mg/g)
		Initial	Equilibrium	
Lala clam shell	MB	5	0.67	0.43
		20	1.51	1.84
		100	2.02	9.78
	RB	5	2.86	0.21
		20	10.32	0.96
		100	12.33	8.75
	MO	5	4.21	0.07
		20	14.31	0.56
		100	57.23	4.27
	CR	5	4.72	0.02
		20	18.95	0.10
		100	59.13	4.08
Activated carbon derived from mangrove stem	MB	5	0.54	0.44
		20	1.50	1.84
		100	2.70	9.70
	RB	5	2.06	0.29
		20	10.54	0.94
		100	15.44	8.44
	MO	5	4.96	0.01
		20	15.28	0.47
		100	61.52	3.84
	CR	5	4.91	0.01
		20	19.29	0.07
		100	64.81	3.51

Adsorption studies. Mix-dye system. It is important to study the potential of lala clam shells to adsorb dyes in the mix-dye system because of their general existence in real water and wastewater. In this study, four dyes were mixed at different initial concentrations of 5, 20 and 100 mg/L. All experiments were performed with 0.5 g of lala clam shells. Table 4 shows the amount of MB, RB, MO and CR adsorbed onto lala clam shells at different initial dye concentration of 5, 20 and 100 mg/L.

It was noticed that the amount of MB, RB and MO adsorbed were convergent somewhat in both the single and mix-dye systems at different initial concentration of 5, 20 and 100 mg/L. A different amount of adsorption was observed for CR. The amount of CR adsorbed by lala clam shells decreased from 0.48, 1.92 and 9.75 mg/g (single-dye system) to 0.02, 0.08 and 3.90 mg/g (mix-dye system) at initial concentration of 5, 20 and 100 mg/L, respectively. The ability of lala clam shells to adsorb dyes in the mix-dye system was in the order of MB > RB > MO > CR, meanwhile a different trend was obtained for single-dye system of which the order was CR > MB > RB > MO.

It was observed that the amount of CR adsorbed became last in the order of the mix-dye system. This can be explained by two main factors: (1) for mix-dye system, the experiment was not performed at the optimum pH value of each dye, which purposely to mimic real wastewater environment, and (2) CR is an anionic dye that possess a negative charge and larger size as compared to MO. In contrast, MB is the cationic dye that has a positive charge and smaller size than RB, which might lead to a stronger affinity with the negatively charge of lala clam shells. The impacts of the competing ions observed in the present study are also relevant to the earlier reports [55-57].

Besides, Table 5 shows the comparison of the amount of dyes adsorbed by lala clam shells and activated carbon derived from mangrove stem in the mix-system. From Table 5, it was clear that MB was the best dye adsorbed by both adsorbents in the mix-system, in the order of MB > RB > MO > CR. The results suggest that lala clam shells have a good potential and can replace activated carbon to remove dyes from wastewater. For example, with 100 mg/L of initial concentration of dyes at the equilibrium, the concentration was decreased to 2.02, 12.33, 57.23 and 59.13 mg/L for MB, RB, MO and CR, respectively. It was observed that the equilibrium concentration became less than 50% for cationic dyes and about 50% for anionic dyes following treatment with lala clam shells, indicates a great potential for future applications.

Characterisation studies. Surface area and pore diameter. The surface area, pore volume and pore diameter of lala clam shells were measured as 2.09 m^2/g, 0.164 cm^3/g and 0.147 nm, respectively. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the pore of the lala clam shells is considered as micropores (d < 2 nm).

FTIR analysis. FTIR is an effective analytical instrument for identifying functional groups and characterising covalent bonding information. The FTIR spectra of the lala clam shells, before and after the adsorption of dyes are shown in Figure 5. Based on Figure 5, the two prominent bands appeared at 1448 cm^{-1} and 853 cm^{-1} are the characteristics of carbonate (CO_3^{2-}) [58]. The band at 1781 cm^{-1} can be assigned to carbonyl (C=O) groups. There were significant changes in the FTIR spectrum of lala clam shells after interaction with dyes. For example, the absorption band of CO_3^{2-} group at 1448 cm^{-1} shifted to 1444, 1464, 1462 and 1467 cm^{-1} following the interaction with CR, MO, MB and RB. In addition, the absorption intensity of this band decreased after the adsorption of MB. Presumably, the shift in wavenumber of the functional groups may be due to the interaction of dyes with active sites of the adsorbent [59]. A new peak observed at 2630 cm^{-1} after interaction with MO can be assigned to C-H stretching. Overall, it is evident from FTIR analysis that carbonate group is the main adsorption site in lala clam shells.

FESEM analysis. FESEM analysis was performed to observe the surface morphology of the lala clam shells before and after the interaction with dyes. The analysis is also useful for determining the particle shape. The FESEM images of lala clam shells before and after being loaded with CR, MO, MB and RB at 10,000x magnifications are shown in Figures 6. Lala clam shells have an uneven structure with non-uniform size distribution on the surface (Figure 6(a)). Subsequent interaction with dyes, the surface of lala clam shells became rough, more uneven and heterogeneous (Figures 6(b), 6(c), 6(d) and 6(e)). The change in the surface morphology of lala clam shells could be due to the reorganisation of surface functional groups binding the CR, MO, MB and RB molecules [60]. From Figure 6(d), it is clear that lala clam shells are covered by MB molecules adsorbed. A similar observation was reported by Su et al. [27] for adsorption of MB onto *Imperata cylindrica* (Cogon grass).

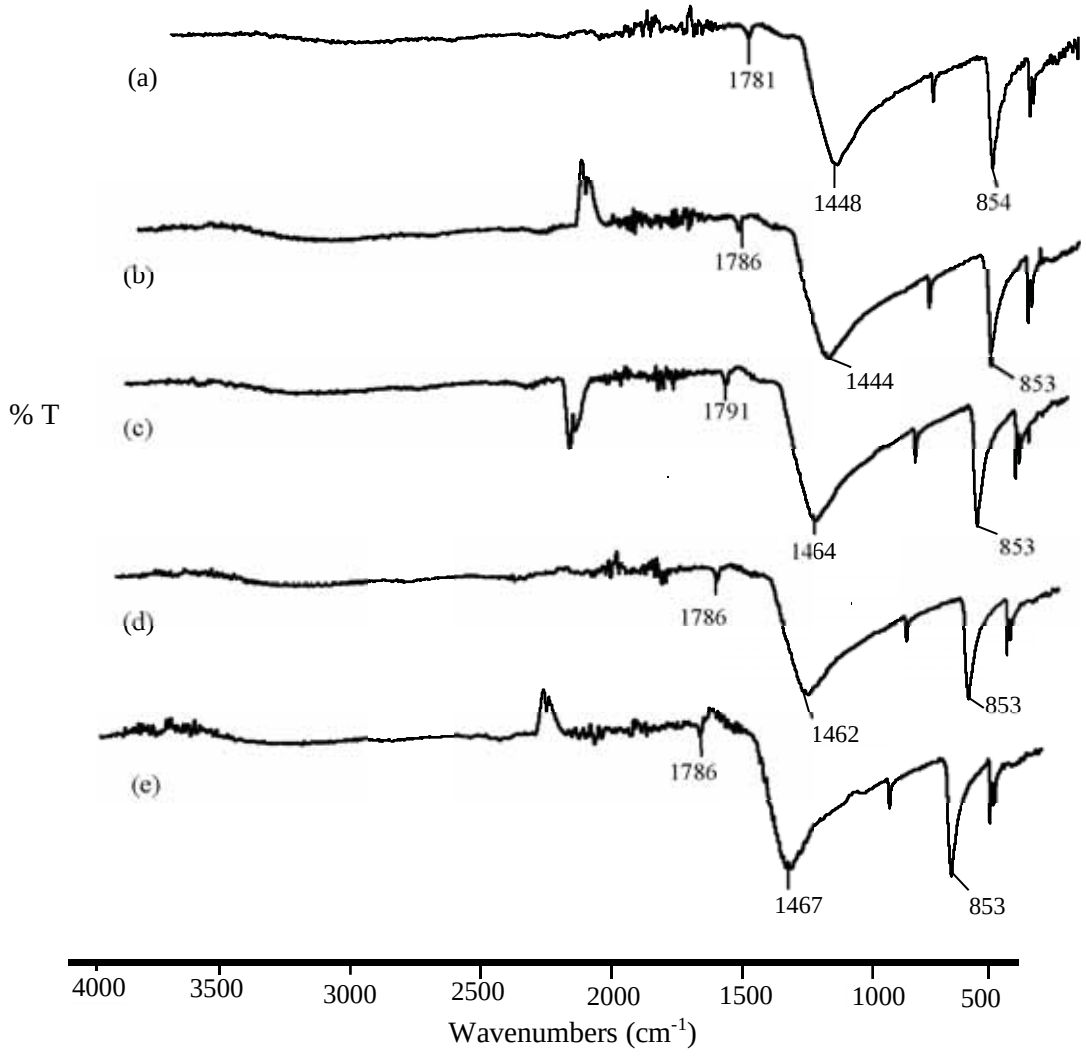


FIGURE 5
The FTIR spectra of lala clam shell (a) before and after adsorption of (b) CR, (c) MO, (d) MB and (e) RB.

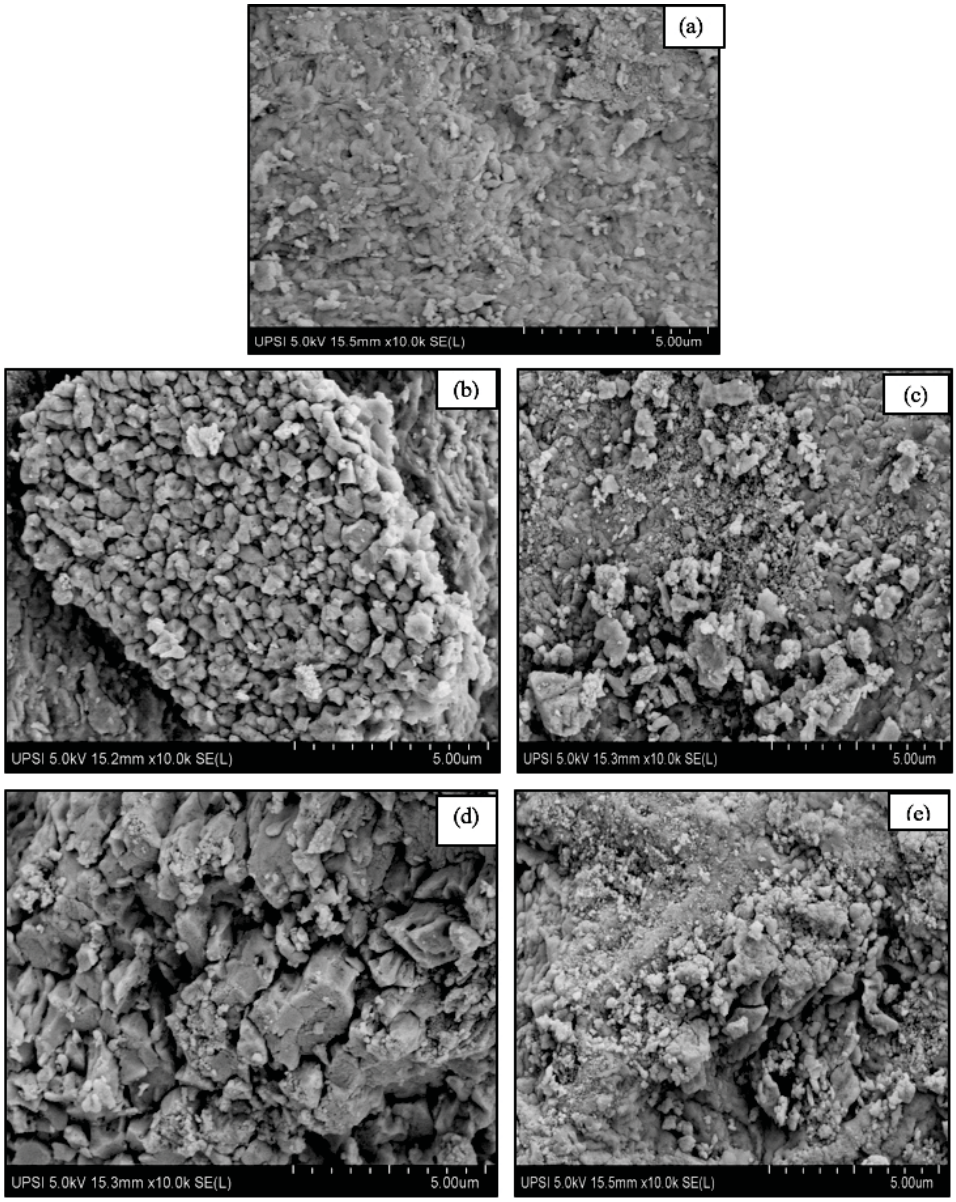


FIGURE 6
FESEM images of lala clam shell before dye adsorption (a) and after adsorption of CR (b), MO (c), MB (d) and RB (e) at 10, 000× magnification.

CONCLUSIONS

As elucidated throughout the study, lala clam shells have several significant advantages over established adsorbents for water treatment. Most notably advantages are abundant availability and good performance, which can be used as an alternative low-cost adsorbent for the removal of dyes from aqueous solution. Its key property is the presence of carbonate group (CO_3^{2-}) that can bind functional groups of dyes during the adsorption process. The adsorption process is greatly influenced by several experimental parameters such as the pH solution, initial dye concentration and adsorbent dosage. The order of selective adsorptions was different in the single- or mix-dye system. The equilibrium data fitted very well with the Freundlich isotherm equation. The adsorption performance of lala clam shells was comparable with mangrove stem derived activated carbon, a commercial adsorbent used in water treatment. Therefore, the developed adsorption treatment system is useful and applicable for the removal of organic dyes from contaminated water.

ACKNOWLEDGEMENTS

The authors would like to Miss Siti Najiah Mohd Yusoff, Mrs. Johana Jumiran, Mr. Mohd Zurin Mahmood, Mr. Ibrahim Saidin and Mr. Hashimi Ma'ani for their technical assistance.

REFERENCES

[1] Jabeen, A., Huang, X.S. and Aamir, M. (2015) The challenges of water pollution, threat to public health, flaws of water laws and policies in Pakistan. J. Water Res. Prot. 7, 1516-1526.

[2] WHO (World Health Organization). (2002) Environmental Health, Eastern Mediterranean Regional Center for Environmental Health Activities (CEHA).

[3] lnyinbor, A.A., Adekol, F.A. and Olatunji, G.A. (2016) Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto *Raphia hookerie* fruit epicarp. Water Res. Ind. 15, 14-27.

[4] Salpekar, A. (2008) Water Pollution. Jnanada prakashan (P & D). New Delhi, India.

[5] Velmurugan, P., Shim, J. and Oh, B.T. (2016) Removal of anionic dye using amine-functionalized mesoporous hollow shells prepared from corn cob silica. Res. Chem. Intermed. 42, 5937-5950.

[6] Terangpi, P. and Chakraborty, S. (2017) Adsorption kinetics and equilibrium studies for removal of acid azo dyes by aniline formaldehyde condensate. App. Water Sci. 7(7), 3661-3671.

[7] Zheng, L., Wang, C., Shu, Y., Yan, X. and Li, L. (2016) Utilization of diatomite/chitosan–Fe (III) composite for the removal of anionic azo dyes from wastewater: Equilibrium, kinetics and thermodynamics. Colloids Surf. A. 468, 129-139.

[8] Boudechiche, N., Mokaddem, H., Sadaoui, Z. and Trari, M. (2016) Biosorption of cationic dye from aqueous solutions onto lignocellulosic biomass (*Luffa cylindrica*): characterization, equilibrium, kinetic and thermodynamic studies. Int. J. Ind. Chem. 7, 167-180.

[9] Zhu, W., Liu, L., Liao, Q., Chen, X., Qian, Z., Shen, J., Liang, J. and Yao, J. (2016) Functionalization of cellulose with hyperbranched polyethylenimine for selective dye adsorption and separation. Cellulose. 23(6), 3785-3797.

[10] Liu, G., Hu, Z., Guan, R., Zhao, Y., Zhang, H. and Zhang, B. (2016) Efficient removal of methylene blue in aqueous solution by freeze-dried calcium alginate beads. Korean J. Chem. Eng. 33(11), 3141-3148.

[11] Cheng, M., Zeng, G., Huang, D., Lai, C., Wei, Z., Li, N., Xu, P., Zhang, C., Zhu, Y. and He, X. (2015) Combined biological removal of methylene blue from aqueous solutions using rice straw and *Phanerochaete chrysosporium.* Appl. Microbiol. Biotechnol. 99, 5247-5256.

[12] Liang, C.Z., Sun, S.P., Li, F.Y., Ong, Y.K. and Chung, T.S. (2014) Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation / flocculation and nanofiltration. J. Membr. Sci. 469, 306-315.

[13] Brillas, E. and Martinez-Huitle, C.A. (2015) Decontamination of wastewater containing synthetic organic dyes by electrochemical methods an updated review. Appl. Catal. B: Environ. 166-167, 603-643.

[14] Păcurariu, C., Paska, O., Ianos, R. and Muntean, S.G. (2016) Effective removal of methylene blue from aqueous solution using a new magnetic iron oxide nanosorbent prepared by combustion synthesis. Clean Tech. Environ. Policy. 18, 705–715.

[15] Carmona, E.N., Soprani, M. and Sberveglieri, V. (2017) Nanowire (S3) Device for the quality control of drinking water. Measurement and Instrumentation. 23, 179-197.

[16] Ceskaa. (2015) Global Activated Carbon Market: 2014-2019. Available at: https://ceskaa.com/shop/advanced-materials/global-activated-carbon-market/.

[17] Amode, J.O., Santos, J.H., Alam, Z.M., Mirza, A.H. and Mei, C.C. (2016) Adsorption of methylene blue from aqueous solution using untreated and treated (Metroxylon spp.) waste adsorbent: equilibrium and kinetics studies. Int. J. Ind. Chem. 7, 333-345.

[18] Mahmoud, G.A., Abdel-Aal, S.E., Badway, N.A., Elbayaa, A.A. and Ahmed, D.F. (2017) A novel hydrogel based on agricultural waste for removal of hazardous dyes from aqueous solution and reuse process in a secondary adsorption. Polym. Bull. 74(2), 337-358.

[19] Taufiq-Yap, Y.H., Lee, H.V. and Lau, P.L. (2012) Transesterification of jatropha curcas oil to biodiesel by using short necked clam (*Orbicularia orbiculata*) shell derived catalyst. Energy Explor. Exploit. 30(5), 853-866.

[20] Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309-319.

[21] 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.

[22] Güzel, F., Sayğili, H., Sayğili, G.A. and Koyunca, F. (2015) New low-cost nanoporous carbonaceous adsorbent developed from carob (Ceratonia siliqua) processing industry waste for the adsorption of anionic textile dye: Characterization, equilibrium and kinetic modelling. J. Mol. Liq. 206, 244-255.

[23] Si, J., Yuan, T.Q. and Cui, B.K. (2015) Exploring strategies for adsorption of azo dye Congo Red using free and immobilized biomasses of Trametes pubescens. Ann Microbiol. 65, 411-421.

[24] Umpuch, C. and Sakaew, S. (2013) Removal of methyl orange from aqueous solutions by adsorption using chitosan intercalated montmorillonite. Songklanakarin J. Sci. Technol. 35(4), 451-459.

[25] Mahmoudi, K., Hosni, K., Hamdi, N. and Srasra, E. (2015) Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits-A comparative study. Korean J. Chem. Eng. 32(2), 274-283.

[26] Uddin, M.T., Islam, M.A., Mahmud, S. and Rukanuzzaman, M. (2009) Adsorptive removal of methylene blue by tea waste. J. Hazard Mater. 164, 53-60.

[27] Su, C.X.H., Teng, T.T., Alkarkhi, A.F.M. and Low, L.W. (2014) *Imperata cylindrica* (Cogongrass) as an Adsorbent for Methylene Blue Dye Removal: Process Optimization. Water Air Soil Poll. 225,1941, 1-12.

[28] Zeng, L. and Yang, L. (2015) Preparation and Characterization of Ni-Doped Calcium Silicate Hydrate Based on Steel Slag: Adsorption Capacity for Rhodamine B from aqueous Solution. J. Chem. 2015, 9p.

[29] Fathy, N.A., El-Shafey, O.I. and Khalil, L.B. (2013) Effectiveness of Alkali-Acid Treatment in Enhancement the Adsorption Capacity for Rice Straw: The Removal of Methylene Blue Dye. ISRN Phys. Chem. 2013, 15p.

[30] Betowski, L.D., Yinon, J. and Voyksner, R.D. (1995) Mass spectrometry in the analysis of dyes in wastewater. In: Reife, A., Freeman, H.S. (eds.) Environmental Chemistry of Dyes and pigments. John Wiley and Sons, Inc. Canada.

[31] Sharma, P. and Kaur, H. (2011) Sugarcane bagasse for the removal of erythrosin B and methylene blue from aqueous waste. Appl. Water Sci. 1, 135-145.

[32] Anna, B., Kleopas, M., Constantine, S., Anestis, F. and Maria, B. (2015) Adsorption of Cd (II), Cu (II), Ni (II) and Pb (II) onto natural bentonite: study in mono-and multi-metal systems. Environ. Earth Sci. 73(9), 5435-5444.

[33] Mondal, N.K., Das, K., Das, B. and Sadhukhan, B. (2016) Effective utilization of calcareous soil towards the removal of methylene blue from aqueous solution. Clean Technol. Envir. 18, 867-881.

[34] Mukhlish, M.Z.B., Khan, M.R., Bhoumick, M.C. and Paul, S. (2012) Papaya (*Carica papaya* L.) Leaf Powder: Novel Adsorbent for Removal of Methylene Blue from Aqueous Solution. Water Air Soil Poll. 223, 4949-4958.

[35] Haitham, K., Razak, S., and Nawi, M.A. (2018) Kinetics and isotherm studies of methyl orange adsorption by a highly recyclable immobilized polyaniline on a glass plate. Arab. J. Chem. (in press).

[36] Dey, M.D., Shukla, R., Bordoloi, N.K. Doley, R. and Mukhopadhyay, R. (2015) Mechanism of Adsorptive Removal of Methylene Blue Using Dried Biomass of *Rhizopus oryzae*. Appl. Biochem. Biotechnol. 177, 541–555.

[37] Yaneva, Z.L. and Georgieva, N.V. (2012) Insights into Congo Red Adsorption on Agro-Industrial Materials- Spectral, Equilibrium, Kinetic, Thermodynamic, Dynamic and Desorption Studies. A Review. Int. Rev. Chem. Eng. 4, 127-145.

[38] Movahedi, M., Mahjoub, A.R. and Darzi, S.J. (2009) Photodegradation of Congo Red in Aqueous Solution on ZnO as an Alternative Catalyst to TiO_2. J. Iran Chem. Soc. 6(3), 570-577.

[39] Freundlich, H.M.F. (1906) Uber Die Adsorption in Lasungen. J. Phys. Chem. 57, 385-470.

[40] Langmuir, I. (1916) The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. J. Am. Chem. Soc. 38, 2221-2295.

[41] Balasubramani, K. and Sivarajasekar, N. (2014) Adsorption studies of organic pollutants onto activated carbon. Int. J. Innov. Res. Sci. Eng. Tech. 3(3), 10575-10581.

[42] Hall, K.R., Eagleton, L.C., Acrivos, A., and Vermeulen, T. (1966) Pore-and Solid Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions. Ind. Eng. Chem. Fund. 5, 212-223.

[43] Ogunmodede, O.T., Ojo, A.A., Adewole, E. and Adebayo, O.L. (2015) Adsorptive removal of anionic dye from aqueous solutions by mixture of Kaolin and Bentonite clay: Characteristics, isotherm, kinetic and thermodynamic studies. Iran J. Environ. Eng. 6(2), 147-153.

[44] Fumba, G., Essomba, J.S., Tagne, G. M., Nsami, J.N., Bélibi, P.D.B. and Mbadcam, J. K. (2014) Equilibrium and Kinetic Adsorption Studies of Methyl Orange from Aqueous Solutions Using Kaolinite, Metakaolinite and Activated Geopolymer as Low Cost Adsorbents. J. Acad. Ind. Res. 3, 156-163.

[45] Reddy, D.H.K., Seshaiah, K., Reddy, A.V.R., Rao, M.M. and Wang, M.C. (2010) Biosorption of Pb^{2+} from Aqueous Solutions by Moringa oleifera Bark: Equilibrium and Kinetic Studies. J. Hazard. Mater. 174, 831-838.

[46] Wanyonyi, W.C., Onyari, J.M., and Shiundu, P.M. (2014) Adsorption of Congo Red Dye from Aqueous Solutions Using Roots of *Eichhornia crassipes*: Kinetic and Equilibrium Studies. Energy Procedia. 50, 862 -869.

[47] Abbas, A., Murtaza, S., Kashif, S., Munir, M., Ayub, R. and Akber, S. (2012) Comparative Study of Adsorptive Removal of Congo Red and Brilliant Green Dyes from Water Using Peanut Shell. J. Sci. Res. 11(6), 828-832.
[48] Vimonses, V., Lei, S., Jin, B., Chow, C.W.K. and Saint, C. (2009) Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. Chem. Eng. J. 148, 354-364.
[49] Ozdemir, F.A., Demirata, B. and Apak, R. (2009) Adsorptive removal of methylene blue from simulated dyeing wastewater with melamine-formaldehyde-urea resin. J. Appl. Polym. Sci. 112(6), 3442-3448.
[50] Sarkar, D. and Bandyopadhyay, A. (2010) Adsorptive mass transport of dye on rice husk ash. J. Water Res. Protec. 2, 424-431.
[51] Rehman, M.S.U., Kim, I. and Han, J.I. (2012) Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass. Carbohydr. Polym. 90, 1314-1322.
[52] Pal, J., Deb, M.K., Deshmukh, D.K. and Verma, D. (2013) Removal of methyl orange by activated carbon modified by silver nanoparticles. Appl. Water Sci. 3, 367–374.
[53] Das, S. and Barman, S. (2013) Studies on removal of safanine-t and methyl orange dyes from aqueous solution using NaX zeolite synthesized from fly ash. Int. J. Sci. 2, 735-747.
[54] Subasioglu, T. and Bilkay, I. S. (2009) Determination of biosorption conditions of methyl orange by *Humicol fuscoatra*. J. Sci. Ind. Res. 68, 1075–1077.
[55] Ejhieh, A.N. and Shamsabadi, M.K. (2013) Decolorization of a binary azo dyes mixture using CuO incorporated nanozeolite-X as a heterogeneous catalyst and solar irradiation. Chem. Eng. J. 228, 631-641.
[56] Yi, F.Y., Zhu, W., Dang, S., Li, J.P., Wu, D., Li, Y.H. and Sun, Z.M. (2015) Polyoxometalates-based heterometallic organic–inorganic hybrid materials for rapid adsorption and selective separation of methylene blue from aqueous solutions. Chem. Commun. 51, 3336-3339.
[57] Jones, G.C. and Jackson, B. (1993) Infrared Transmission Spectra of Carbonate Minerals. Springer- Science Business Media B. V, UK.
[58] Yusoff, S.N.M., Kamari, A., Putra, W.P., Ishak, C.F., Mohamed, A., Hashim, N., Isa, I.M. (2014) Removal of Cu (II), Pb (II) and Zn (II) Ions from Aqueous Solutions Using Selected Agricultural Wastes: Adsorption and Characterisation Studies. J. Environ. Prot. 5, 289-300.
[59] Chieng, H.I., Zehra, T., Lim, L.B.L., Priyantha, N. and Tennakoon, D.T.B. (2014) Sorption characteristics of peat of Brunei Darussalam IV: equilibrium, thermodynamics and kinetics of adsorption of methylene blue and malachite green dyes from aqueous solution. Environ. Earth Sci. 72, 2263-2277.

Received: **19.10.2017**
Accepted: **13.03.2018**

CORRESPONDING AUTHOR

Azlan Kamari
Department of Chemistry
Faculty of Science and Mathematics
Universiti Pendidikan Sultan Idris
35900 Perak – Malaysia

e-mail: azlkam@yahoo.co.uk
azlan.kamari@fsmt.upsi.edu.my