Development of Novel Low-Cost Quaternized Adsorbent from Palm Oil Agriculture Waste for Reactive Dye Removal

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An attempt was made to chemically modify palm kernel shell (MPKS) to increase adsorption affinity towards Reactive Black 5 (RB5). Granulated palm kernel shell (PKS) was quaternized successfully by treating with N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride under alkaline conditions and was characterized. Surface characterization by Scanning Electron Microscopy (SEM) and BET analysis confirmed the surface pore enlargement from mesospores to macropores after modification. Fourier Transform-Infrared (FTIR) Spectrometer and CHN analysis revealed that the quaternary ammonia group (NR_4^+) was successfully reacted on MPKS fiber. pH 4 is the optimum for removal of RB5 on MPKS. Equilibrium isotherms were analyzed by the Langmuir, Freundlich, and Redlich-Peterson models. The Redlich-Peterson model was found to fit well with the data. The maximum adsorption capacity of MPKS was 207.5 mg/g for adsorption of RB5.

Keywords: Characterization; Dyes; Isotherm; Low cost adsorbent; Palm kernel shell; Surface chemistry; Quaternization

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INTRODUCTION

Fresh water is in short supply globally, and one of the causes of this situation is poor management of wastewater (Payment 2003). The textile industry discharges more than 280,000 tons of dye-contaminated wastewater into the environment yearly (Jin *et al.* 2007). The batik industry (traditional textile handicraft) is the largest cottage textile industry in Southeast Asia, especially in Malaysia, Indonesia, and Thailand. Reactive azo dyes are the most commonly used synthetic dyes in the batik textile industry for dying cellulosic material such as cotton, silk, flax, and wool (Rashidi *et al*. 2012). The dyes are bright, diverse in color, low in cost, and easier to dye compared to natural dye. However, up to 50% of these anionic dyes, or about 0.6 to 0.8 g dye/dm^3, are lost into spent dye baths due to poor fixation ability (Gahr *et al.* 1994; Kumari and Abraham 2007). Dye-polluted wastewater generated from the textile industry can be expected to drain to rivers and the sea if no proper treatment is done. In Malaysia, industrial effluent must be treated to meet standard as stipulated in the Third Schedule Environmental Quality Act (1974).

The degradation of azo linkages of reactive azo dyes in wastewater causes the release of toxic, mutagenic, carcinogenic, and colorless aromatic amines that threaten public health (Chen 2002; Pinheiro *et al.* 2004; Akceylan *et al*. 2009; Chen *et al.* 2009).

Chung *et al.* (1992). Levine (1991) reported that ingested azo dyes metabolized to aromatic amines in the body by intestinal microorganisms and reductive enzymes in the liver. There have been many cases reported indicating that contact with reactive azo dyes causes severe health problems such as dermatitis, skin cancer (Mirjalili *et al.* 2011), intestinal cancer, and brain abnormalities in fetuses (Doble and Kumar 2005). Furthermore, the reactive azo dye wastewater has great impact on the environment, because it is high in chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Additionally, the xenobiotic and recalcitrant nature of dyes leads to resistance of aerobic digestion, light, and oxidation agents (Meriç *et al.* 2004; Gupta and Suhas 2009). The dye-polluted wastewaters are strongly colored, and, even in low dosages, cause aesthetic problems and reduction in sunlight penetration, thereby inhibiting photosynthesis and destroying aquatic ecosystems. Moreover, a review paper reported by Solís *et al.* (2012) stated that azo dye is an eco-toxin that can inhibit the germination of many plant species. Therefore, treating dye effluent before releasing it to open water is crucial in order to assure enough fresh water for future generations.

There are not many efficient, low cost, and conventional ways to treat synthetic dye-contaminated wastewater. Several physical, chemical, and biological methods such as microorganism degradation, membrane filtration, flocculation or coagulation, ion-exchange, and chemical oxidation have been reported for the removal of dye from wastewater (Banat *et al.* 1996; McMullan *et al.* 2001; Robinson *et al.* 2001; Crini 2006). However, most of the methods have issues including: low treatment efficiency, long treatment duration, large land area requirement, membrane fouling, by-product disposal issues, complicated process designs, high cost, or high energy consumption.

Adsorption is recognized as one of the best and widely used methods for wastewater treatment due to simple equipment and process operations, no harmful by-products, high efficiency, and low energy consumption (Dąbrowski 2001). Coal-based activated carbon is the most common adsorbent used, but it is costly and not sustainable. Abundant low cost agriculture wastes, which contain high amounts of natural polymers such as cellulose, hemicellulose, and lignin, are suitable alternative materials to produce economical and green adsorbents, but modification is necessary to enhance its efficiency (Crini 2006; Gupta and Suhas 2009; Lin and Juang 2009; Rafatullah *et al.* 2010).

The cost for thermal treatment involving carbonization at 300 °C for 60 min followed by activation at 850 °C for 40 min in a furnace is USD 228 per ton of activated carbon (Li *et al.* 2011). These processes require very high electricity consumption and also high cost for equipment such as the furnace. Lima *et al.* (2008) also reported that the electricity cost in producing activated carbon accounts for 63.5% of the total production cost.

Chemical modifications such as mercerization and quaternization of biomass to produce adsorbent can overcome this shortcoming by substituting the high energy consumption steps in activated carbon production with simple chemical reactions. Therefore, the production cost for chemically modified adsorbent can be reduced more than 60% as compared to the use of thermally activated adsorbent.

Quaternization or cationization is a surface chemical treatment that adds a NH_4^+ group onto lignocellulosic fiber via epoxy substitution. Such a group can increase affinity towards anionic substances by promoting ion-exchange adsorption (Orlando *et al.* 2002; Wartelle and Marshall 2006). Quaternized lignocellulosic fiber from agriculture wastes has been studied by previous researchers. Research utilizing quaternized lignocellulosic fiber as an adsorbent to remove anionic substrates is summarized in Table 1. However, there is very little research done on reactive dye removal by these quaternized lignocellulosic fibers and exploration on versatile fiber sources has been needed.

Table 1. Summary of Research Done Using Quaternized Lignocellulosic Biomass as Adsorbent for Removal of Anionic Substrates

Quaternized Biomass	Anionic Substrate	Maximum Adsorption Capacity *qm* (mg/g)	References
Chinese reed	Nitrate	7.6	Namasivayam and Höll (2005)
	Perchlorate	13.3	
	Phosphate	16.6	
	Sulfate	10.1	
Coconut coir pith	Arsenic (V)	13.6	Anirudhan *et al.* (2007)
Coconut shell	Nitrate	33.7	de Lima *et al.* (2012)
	Sulfate	31.2	
	Phosphate	200.0	
Corn stover	Phosphate	62.7	Wartelle and Marshall (2006)
Flax shive	Reactive red 228	190.0	Wang and Li (2013)
Reed	Perchlorate	150.2	Baidas *et al.* (2011)
Maize cobs	Methyl orange	-	Elizalde-González *et al.* (2008)
	Arsenic	-	
Palm kernel shell	Reactive black 5	207.5	This work
Rice husk	Reactive blue 2	130.0	Low and Lee (1997)
Rice hull	Nitrate	80.0	Orlando *et al.* (2002)
Rice straw	Sulphate	74.8	Cao *et al.* (2011)
Soybean hull	Arsenate	72.2	Marshall and Wartelle (2004)
	Chromate	59.8	
	Dichromate	104.0	
	Phosphate	59.8	
	Selenate	51.0	
Sugarcane bagasse	Nitrate	86.8	Orlando *et al.* (2002)
Wheat straw	Nitrate	129.0	Wang *et. al.* (2007)
Wheat straw	Acid Red 73	714.3	Xu *et al.* (2010)
	Reactive red 24	285.7	
Wheat straw	Methylene blue	139.4	Zhang *et al.* (2012)

Malaysia is one of the major world producers of palm oil. As of June 2012, the planted area of oil palms totaled 5.03 million hectares (Malaysia Palm Oil Board 2012). Palm kernel shell (PKS) is one of the wastes from the production of crude palm oil. Figure 1 shows a simplified crude palm oil production flow chart including the waste produced at each step. The estimated composition of palm oil mill waste is 14.6% empty fruit bunch (EFB), 10.4% PKS, 15.4% fiber, and 6.3% palm oil mill effluent (POME) on dry weight of fresh fruit bunch basis (Yusoff 2006). Statistics show that Malaysia produced 5.2 million tons of PKS in 2010 (Ng *et al.* 2012). PKS is a more suitable material as adsorbent than other palm oil biomass due to its high mechanical strength, high density, porous surface, chemical stability, variable surface functional groups, and insolubility in water (Ofomaja 2007; El-Sayed 2011). Nevertheless, research and development on modifying PKS is needed to enhance its adsorption efficiency, especially towards ionic substrates, hence increasing its commercial potential and turning the waste to wealth. The present study aims to develop quaternized PKS as novel adsorbent to remove Reactive Black 5 (RB5) from aqueous solution.

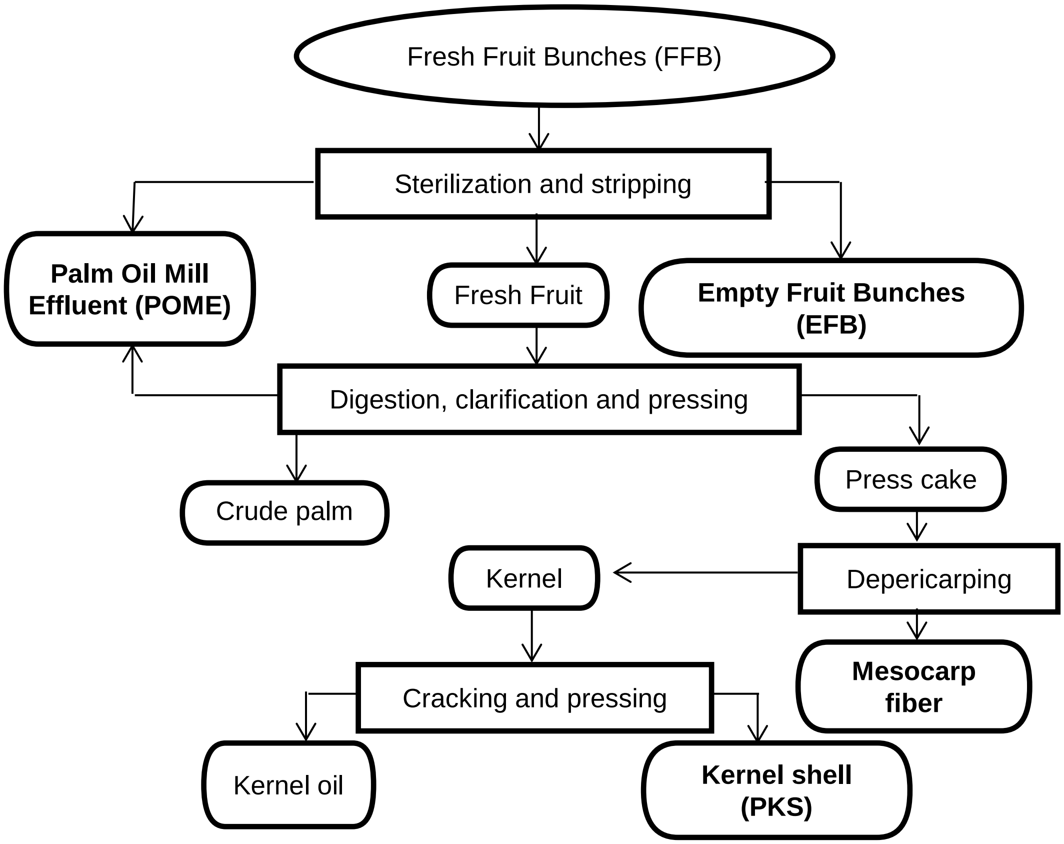


Fig. 1. Crude palm oil production flow diagram in palm oil mill (waste in bold) (Sulaiman *et al.* 2011)

EXPERIMENTAL

Materials

Raw PKS as a by-product of crude palm oil production was obtained from Rompin palm oil mill, Pahang, Malaysia. The reactive dye used in this study was C.I. Reactive Black 5 (RB5), CAS number 17095-24-8 supplied by Texchem-pack, Malaysia without further purification. RB5 has a maximum adsorption wavelength (λ_{max}) of 596 nm. Dye stock solutions of 1000 mg/L were prepared by weighing 1.0000 g (± 0.0005) of dye into a 1 L volumetric flask and dissolving the solids in distilled water. The stock solution would then be diluted to the desired concentration. N-(3-chloro-2-hydroxy-propyl)trimethylammonium chloride (CHMAC) 60% in water was purchased from Sigma-Aldrich. NaOH was purchased from Merck. Acetone, acetic acid, and hydrochloric acid were all analytical grade purchased from Acros. All chemicals were used without further purification.

Methods

Preparation of raw PKS

PKS was rinsed with hot water followed by acetone to remove oil and dried under the sun. Then, raw PKS was ground and sieved to size between 1 to 0.25 mm. Granular PKS was mercerized by soaking in NaOH of 20, 40, and 60 wt%, respectively, for 10 h at room temperature to determine the best concentration. Mercerized PKS was rinsed with distilled water and dried at 60 °C. The study on effect of NaOH solution concentration during mercerization is important to get optimum quaternization reaction yield.

Quaternization of PKS

Dried mercerized PKS was weighed. Each gram of PKS was reacted with a reaction mixture consisting of 1.5: 4: 2.5 wt./wt. ratio of NaOH, CHMAC, and water, respectively. Hence, the reaction mixture contained 37 mmol of NaOH and 35 mmol of CHMAC per gram of PKS contained. The mixture was left at room temperature for 24 hours. Then, the modified PKS (MPKS) was rinsed with 0.2% acetic acid solution to halt the reaction, followed by distilled water until pH 7 was achieved. Granular MPKS was dried at 60 °C and was kept in desiccator.

Characterization of MPKS

Surface morphology was imaged using Scanning Electron Microscopy (SEM) (Hitachi S-3400N) to observe the adsorbent surface pore size. Samples were coated with a thin layer of Au/Pd. The SEM device was operated at 5 kV, and scanning electron photographs were recorded at a magnification of 1000X to 5000X depending on the nature of the sample.

Specific surface area was measured by BET surface area analyzer (AutoSorb-1 Quantachrome). Pore size distribution, average pore size, and pore volume of samples were determined using the Barrett, Johner, and Halenda (BJH) equation.

Infrared (IR) spectra were recorded on a Fourier Transform-Infrared (FT-IR) Spectrometer (Perkin Elmer 1750X). The sampling technique used was attenuated total reflectance (ATR). All the spectra were plotted as the percentage of transmittance versus wave number (cm^{-1}) for the range of 400 to 4000 cm^{-1} at room temperature. Functional groups of samples were determined from the FTIR spectrum. Hence, detection of quaternary amine group in the spectra will serve as evidence for success quaternization treatment.

Nitrogen content of MPKS was determined using a CHN elemental analyzer (LECO CHNS-932). It was assumed that percentage of nitrogen obtained represents the grafted amine groups contain on MPKS. The cationic group added in MPKS and percentage of reaction efficiency was determined by Eqs. 1 and 2, respectively,

$$\text{Cationic group added (mmol N/g)} = (\%\ N_{MPKS} - \%\ N_{PKS}) \text{ X } 10/\ Ar_{N} \qquad (1)$$

$$\text{Reaction efficiency (\%)} = (\text{cationic group added}) / 35 \text{ X } 100 \qquad (2)$$

where, Ar_N is the relative atomic mass of nitrogen, and the factor 35 is the mmol of CHMAC added to reaction mixture, which represents nitrogen (N) added per gram of PKS (Marshall and Wartelle 2004).

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer. About 10 mg of sample was used for analysis and was subjected to a constant heating rate of 10 °C per min from 28 °C to 500 °C in a nitrogen environment with flow rate of 20 mL per min. The weight loss during heating was recorded and analyzed.

X-Ray Diffraction (XRD) was performed by Shimadzu XRD-6000 X-ray diffractometer to determine its structure and percentage of crystallinity. The X-ray beam was nickel filtered Cu Kα (λ = 1.542 Å) radiation operated at 30 kV and 30 mA. Diffraction data were recorded with scattering angles (2θ) ranging from 0 ° to 45 ° at a rate of 2 ° per min.

The procedure to determine proximate chemical composition such as cellulose, hemicellulose, and lignin of PKS and MPKS was based on wood industry sector method as reported in Carrier *et al.* (2011).

Surface chemistry was acquired using the Boehm titration method (Boehm 1994). 0.1 g of sorbent was placed into four 100 mL flasks containing 50 mL of 0.1 N Na_2CO_3, $NaHCO_3$, NaOH, and HCl solution, respectively. The flasks were sealed and shaken for 3 days. Then the solution was filtered. Ten milliliters of the filtrate was pipetted. If the filtrate solution was acidic, then it was titrated with 0.1 N NaOH and 0.1 N HCl if basic.

Eight Erlenmeyer flasks were prepared. 100 mL of 0.01 M $NaNO_3$ solution was placed into each flask and pH of each flask was adjusted to pH 2, 3, 4, 5, 6, 7, 8, and 9, respectively, by adding HCl 0.1 N or NaOH 0.1 N solution. MPKS of 0.1 g was added into each flask. The flasks were sealed and shaken for three days at room temperature. Then final pH was recorded. The point zero charge (pH_{pzc}) of MPKS was determined at the point where difference of pH (Δ pH) is zero (Prahas *et al.* 2008).

Adsorption experiments

All the experiments were completed in batch systems using 250 mL Erlenmeyer flasks. In each flask, the volume of dye was 100 mL, and the dosage of MPKS used was 1 g/L. All flasks were sealed properly to prevent leakage and evaporation. The shaking rate was set at 160 rpm (± 2 rpm) and at a temperature of 28 ˚C (± 2 °C) for all adsorption experiments. RB5 solution was adjusted by using 0.1 N HCl to the desired pH.

The dye concentration was evaluated using a ultraviolet double beam spectrophotometer (GENEYES 10 ultraviolet, U.S.A) at the maximum wavelength of 596 nm. The dye solution was filtered through filter paper to separate the adsorbent before running the UV spectrophotometer analysis.

Adsorption experiments were done to determine the effect of NaOH concentration during mercerization on removal efficiency of MPKS. RB5 solution at an initial concentration of 100 mg/L was prepared, and 1 g/L of MPKS mercerized with NaOH concentrations of 20, 40, and 60 wt% was added to each flask, respectively. All flasks were shaken for 8 hours to reach adsorption equilibrium. The MPKS with optimum removal efficiency was used for the characterization and isotherm study.

The pH meter (B729 Eutect-Singapore) was calibrated using buffer solutions of pH 4.0, 7.0, and 10.0 to prevent error. Initial pHs of 100 mg/L RB5 solutions were adjusted to pH 2, 3, 4, 5, 6, 7, 8, and 9, respectively. Then, 1 g/L of MPKS was added to each flask, which was then shaken for 1.5 hours. The initial pH with optimum dye removal was used for isotherm study.

An adsorption isotherm study on MPKS for removal of RB5 was carried out. Solutions with initial concentrations of 100, 200, 300, 400, 500, 600, 700, and 800 mg/L of RB5 were prepared. 1 g/L of MPKS was added to each flask, which was shaken for 8 days before recording the concentration at equilibrium state. Experiments were repeated triplet. Adsorption capacity q_e was calculated by using Eq. 3,

$$q_e = (C_o - C_e)\, V/m \tag{3}$$

where q_e is the adsorption capacity per gram of MPKS, C_o and C_e are dye concentration in the bulk solution at initial and equilibrium state respectively, V is sample volume, and m is mass of adsorbent.

There were three isotherm models used in this study namely the Langmuir (Eq. 4), Freundlich (Eq. 5), and Redlich-Peterson (Eq.6) isotherm models,

$$q_e = K_L C_e / (1+\alpha_L C_e) \tag{4}$$

$$q_e = K_F C_e^{1/nF} \tag{5}$$

$$q_e = K_R / (1+\alpha_R C_e^{\beta}) \tag{6}$$

where, q_e is adsorption capacity, C_e is dye concentration in the bulk solution equilibrium, K_L and α_L are Langmuir constants, K_F and n_F are Freundlich constants, and K_R, α_R , and β are Redlich-Peterson constants.

Theoretically, the maximum adsorption capacity, q_m, of adsorption system was calculated using Eq. 7,

$$q_m = K / \alpha \tag{7}$$

where q_m is the maximum adsorption capacity of adsorbent, and K and α are Langmuir isotherm parameters.

RESULTS AND DISCUSSION

Characterization

Textural analysis

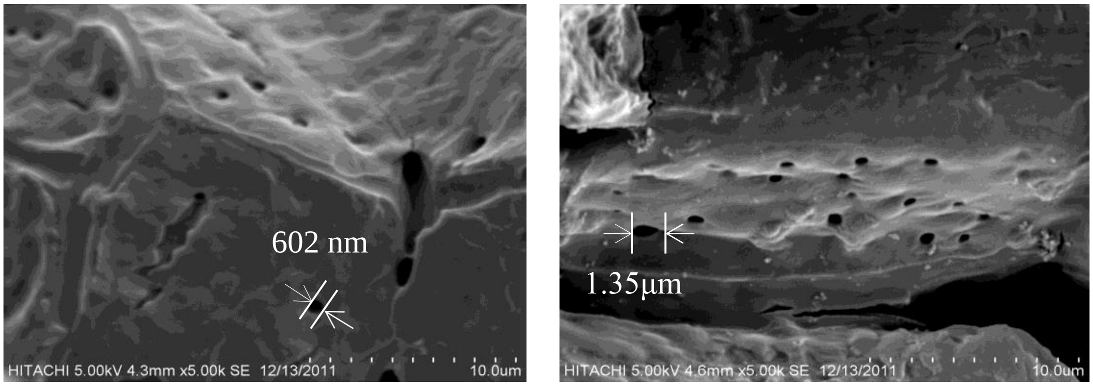
The textural structure of granular PKS and MPKS were observed by SEM images (Fig. 2(a)-(f)). Distinguished dark spots in the micrographs indicate the depth of the pore. Figure 2(a)-(c) shows mercerized PKS with 20 wt%, 40 wt%, and 60 wt% NaOH, respectively, under 5K magnification. From the figures it is apparent that increasing NaOH concentration increased the diameter and number of pores. In Fig. 2 (c), the enlargement of pores had turned into cleavages, exposing more native cellulose so that the previously unreachable inner part of the fiber was able to react with the quaternizing agent. Larger pores also are more suitable for adsorption of bulky substrates such as reactive dyes (Nakagawa *et al.* 2004).

Figure 2(f) shows that after treatment the surface of the MPKS became smoother and more porous compared to PKS (Fig. 2(e)); this might due to the dissolution of impurities and lignin under alkaline solutions in NaOH. In Fig. 2(d), dye molecules were adsorbed on the pores on MPKS after adsorption; hence the pores are less visible.

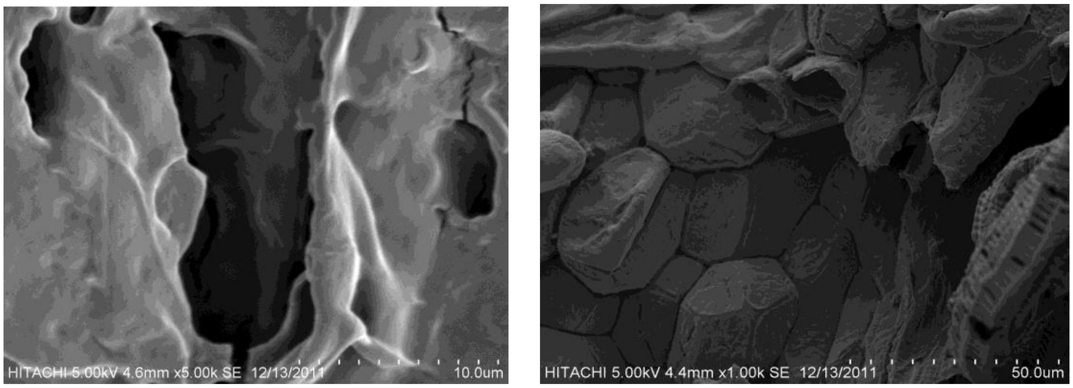
The quantitative data on MPKS pore size was determined using BET analysis. As illustrated in Table 2, the surface of PKS was comprised of mesopores with average pore diameter of 2.2 nm, while after treatment, MPKS had an average pore diameter of 112.6 nm, which is a macropore. The enlargement of pore size is due to degradation of lignin and hemicellulose during the mercerization process. From multi-point BET test, it was observed that the surface area (S_{BET}) and pore volume of MPKS decreased as compared to raw PKS. The slight decrease in surface area after reaction was attributed to the smoother texture of shell surface and enlargement of pore size.

Table 2. Textural Characteristics of PKS and MPKS

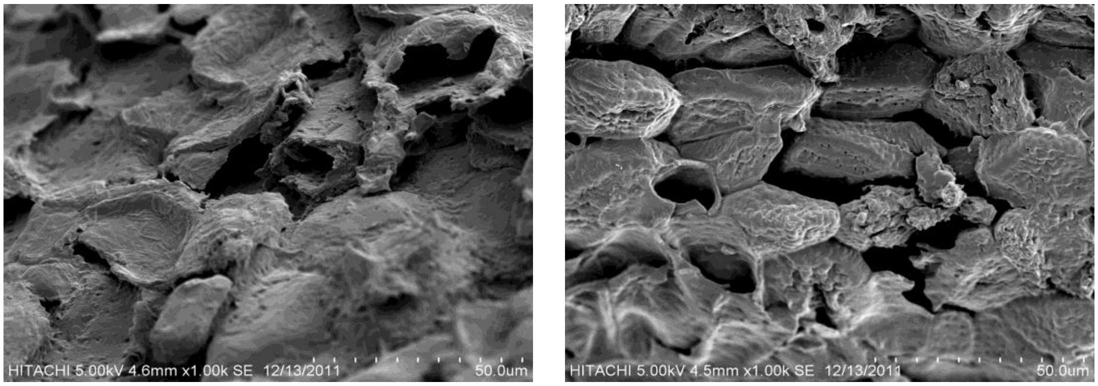
Samples	S_{BET} (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)	% of Pore volume in in stated pore size range (nm)		
				<2	2-50	>50
PKS	1.932	2.2	0.003	0	64.68	35.32
MPKS	1.717	112.6	0.001	0	0	100



(a) 20% NaOH (b) 40% NaOH



(c) 60% NaOH (d) MPKS (After adsorption)



(e) PKS (f) MPKS (Before assorption)

Fig. 2. SEM micrographs of mercerized PKS for (a), (b), and (c) at 5K magnification; and

(d), (e), (f) at 1K magnification

Quaternary amine analysis

FTIR spectra of PKS and MPKS showed that the NR_4^+ group was successfully reacted on MPKS (Fig. 3). The peak at 935 cm^{-1} in the MPKS spectrum that was attributed to C-N stretching was absent in the PKS spectrum. Peaks at 1462 cm^{-1} and 1420 cm^{-1} with nearly equal intensity were assigned to C-H stretching of tert-butyl groups from CHMAC on MPKS. The C-O stretching mode in C-O-C glycosidic linkages appeared at 1030 cm^{-1} and 1033 cm^{-1} for PKS and MPKS, respectively. In addition, PKS and MPKS have O-H stretching bands at 3353 cm^{-1} and 3297 cm^{-1} and C-H stretching at 2923 and 2902 cm^{-1}, respectively. The PKS spectrum shows weak combination bands between 2500 cm^{-1} and 2000 cm^{-1} that are associated with the aromatic rings of lignin structures. Furthermore, the peaks at 1727 cm^{-1} and 1597 cm^{-1} on the PKS spectrum can be assigned to aromatic C=C stretching.

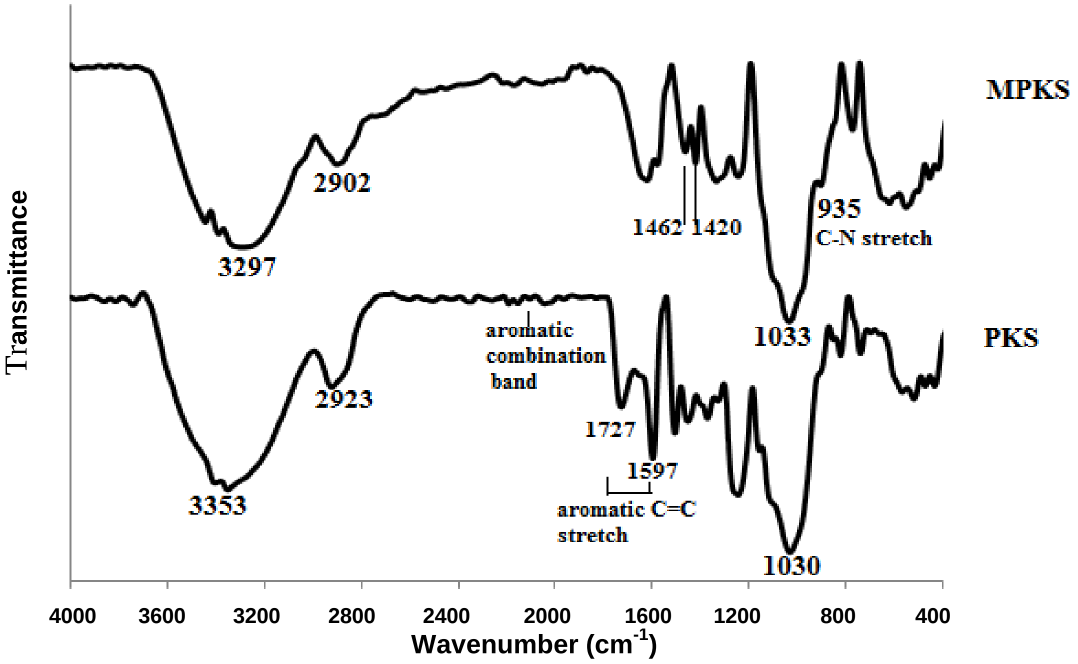


Fig. 3. FTIR spectra of PKS and MPKS

Besides the FTIR analysis, from CHN elemental analysis (Table 3), the nitrogen percentage was increased by 0.74% after quaternization, indicating that the cationic group (NR_4^+) was present in MPKS, confirming that the quaternization treatment on PKS had been successful. Based on Eq. 1, 0.53 mmol of nitrogen was added per gram of MPKS. The reaction efficiency was 1.5% as calculated by using Eq. 2. Furthermore, the MPKS sulfur and nitrogen contents were important indications when dealing with the disposal of waste adsorbent. From CHN analysis, the percentage of nitrogen and sulfur of waste MPKS had become 1.28% and 0.55%. Therefore, incineration cannot be regarded as an appropriate disposal method for waste MPKS, and other methods such as biodegrading would be more suitable.

PKS composition analysis

Results of proximate chemical composition for PKS and MPKS, as shown in Table 3, were based on dry weight basis. After quaternization, the lignin content had decreased the most (12.2%), followed by hemicellulose (8.5%) and cellulose (1.7%). Lignin and hemicellulose were degraded inevitably in NaOH solution during mercerize-tion and quaternization reaction because of their branched and amorphous nature.

Table 3. Proximate Analysis, Elemental Analysis, and Chemical Composition of PKS and MPKS

Proximate Analysis (wt.% dry)	PKS	MPKS
Moisture	4	8
Volatile matter	63	61
Fixed carbon and ash	32	30
Elemental analysis (%)		
Carbon	47.24	45.08
Hydrogen	4.87	5.41
Nitrogen	0.24	0.98
Sulfur	0.00	0.12
Chemical composition (wt% dry)		
Cellulose	31.3	28.6
Hemicellulose	23.8	15.3
Lignin	58.9	47.7
Extractives	5.2	4.8

From the TGA thermographs of PKS and MPKS (Fig. 4), three regions were determined. The first region, which indicated a weight loss of about 4 wt% in PKS and about 8 wt% in MPKS at 29 °C to 150 °C, was due to the evaporation of moisture and low boiling point organic matter. The second region at about 200 °C to 400 °C, which accounted for the main weight loss, was due to the decomposition of hemicellulose (250 °C to 300 °C) and cellulose (300 °C to 350 °C). Decomposition of lignin took place over a broad temperature range (200 °C to 500 °C), because of the various oxygen functional groups in its structure that result in different thermal stabilities (Brebu and Vasile 2010). Nevertheless, the decomposition of hemicellulose, cellulose, and lignin was difficult to differentiate distinctively (Kim *et al.* 2010). From DTG (Fig. 4), both PKS and MPKS show 2 pyrolysis steps: 258 °C to 317 °C (28 wt%) and 337 °C to 378 °C (35 wt%) for PKS; 253 °C to 302 °C (26 wt%) and 319 °C to 354 °C (35 wt%) for MPKS.

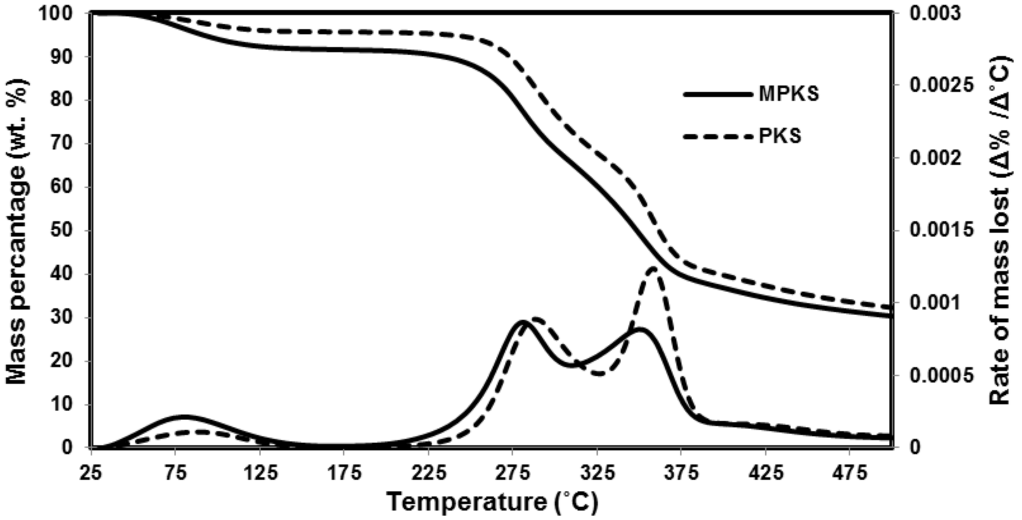


Fig. 4. TGA and DTG curves of PKS and MPKS

The decomposition temperature of MPKS was lower than PKS because of the quaternary ammonium cations (NR_4^+) present in MPKS that catalyzed the decomposition (Gaan *et al.* 2009). The third region (above 400 °C) was due to the decomposition of lignin to char, which happened at a relatively low rate. The residue after 500 °C for PKS and MPKS accounted about 32 wt% and 30 wt%, respectively. Table 3 shows the proximate analysis of PKS and MPKS based on TGA analysis.

The XRD patterns of PKS and MPKS remained the same, indicating that the overall chemical structure and composition of fiber did not change significantly after the surface treatment (Fig. 5). From the peak intensity, it can be concluded that the fiber became slightly amorphous due to the addition of quaternary amine groups on MPKS surface after quaternization. The maximum peak intensity for both PKS and MPKS was at about 22°, and the intensity increased from 796 to 830 after treatment.

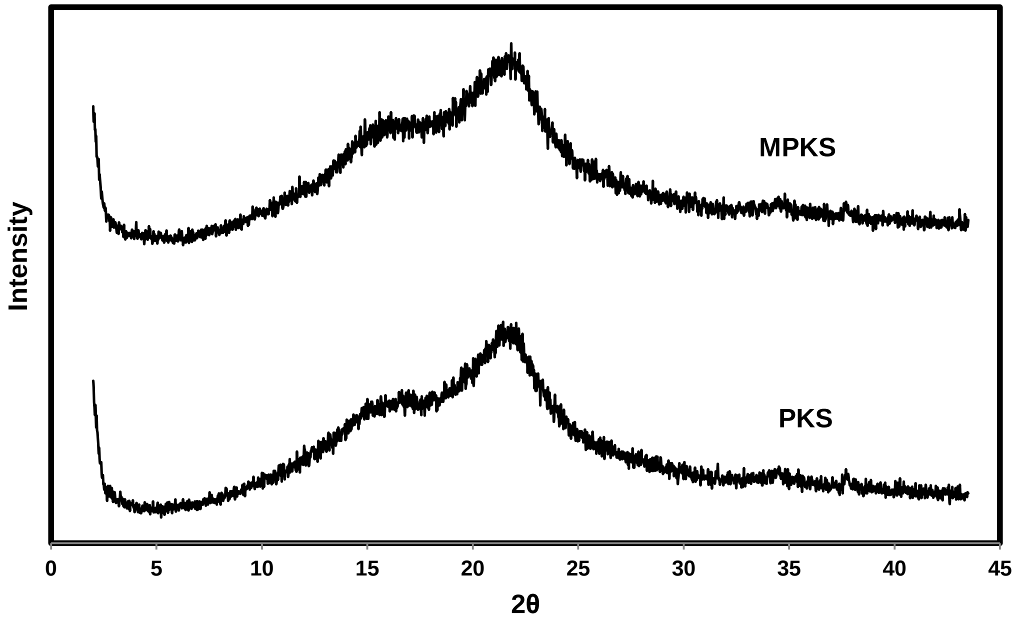


Fig. 5. XRD patterns of PKS and MPKS

From the proximate chemical composition analysis, TGA and XRD analysis for PKS and MPKS, all the tests indicated that in general the composition and structural characteristic of PKS did not exhibit significant changes. Hence it is concluded that quaternization on PKS is only surface treatment.

Surface chemistry analysis

Boehm titration was done to test the surface basicity and acidity before and after the PKS surface treatment. The results from Boehm titration of PKS and MPKS are listed in Table 4. The surface total basicity increased from 0.652 to 1.132 mmol/g after treatment; this can be attributed to the quaternary amine groups, which are Lewis basic functional groups that can donate protons, contributing to the surface basicity. Qiu and Ling (2006) observed that amination on resin increased the surface total basicity, which enhanced the adsorption capacity towards RB5.

Table 4. Surface Chemistry Analysis

Surface Chemistry (mmol /g)	PKS	MPKS
Carboxyls	1.433	1.477
Lactones	0.067	0.118
Phenols	0.186	0.110
Total surface acidity	1.686	1.705
Total surface basicity	0.652	1.132

From Fig. 6, pH_{pzc} was determined to be pH 2.2. Values of pH below the pH_{pzc} resulted in net positive surface charge on adsorbent. The minimum point from the graph occurs at pH 4. Hence, at pH 4 MPKS acquired the most positive surface charge and was the best pH condition to adsorb anionic substances. The initial pH of all adsorption experiments in this study was adjusted to pH 4.

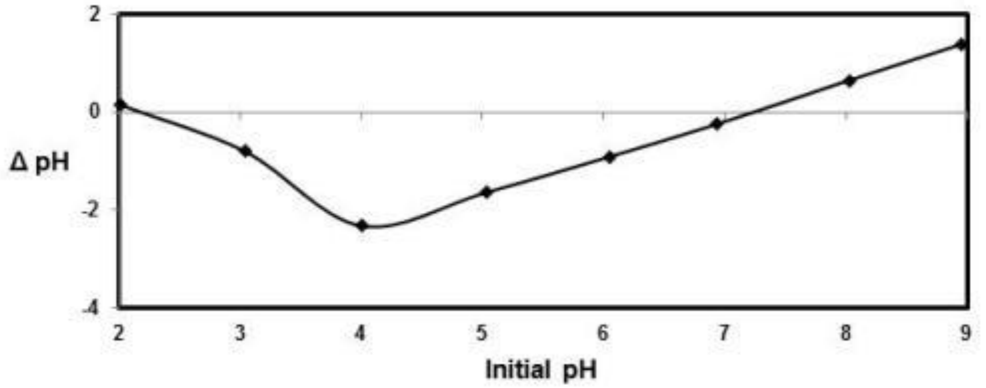


Fig. 6. Point zero charge of MPKS.

Adsorption Experiment

Effect of mercerization

The amorphous phase of fiber is the main adsorption site (Gurgel *et al.* 2008). Goswami *et al.* (2009) reported that fiber treated with increasing sodium hydroxide concentration showed increasing amorphous nature and porosity. In this study, PKS was mercerized by soaking in NaOH solution. The purpose of this pre-treatment step is to make the fiber swell, remove impurities such as lignin, and convert native cellulose into alkaline-cellulose, making the hydroxyl groups more accessible to the subsequent quaternization reaction (Pušić *et al.* 1999).

MPKS with the NaOH concentrations 60, 40, and 20 wt% during mercerization resulted in RB5 dye removal levels of 99%, 26%, and 14%, respectively. Hence, higher NaOH concentration yielded higher removal efficiency. From results of BET and SEM analysis, increasing NaOH concentration during mercerization enlarged the pore size of MPKS to macropores, hence increasing the accessible internal volume of MPKS for adsorption of relatively larger molecules such as reactive dyes (Nakagawa *et al*. 2004). Therefore, MPKS with 60 wt% NaOH for mercerization resulted in the best removability for both reactive dyes. However, NaOH greater than 60 wt% is too viscous with low wetting ability, making it unsuitable for use. Therefore, 60 wt% NaOH solution was used in the mercerization process to prepare all the MPKS for adsorption experiments.

Effect of Initial pH

Figure 7 shows the effect of pH on the removal of RB5 by MPKS. In this study, the optimum pH for adsorption was at pH 4. The maximum removal of RB5 by MPKS after 1.5 h contact time was 79.6%. This experimental result is in agreement with the result from the point of zero charge test on MPKS (Fig. 6). By contrast, pH 9 showed the lowest percentage removal of RB5, which was only 63.8%.

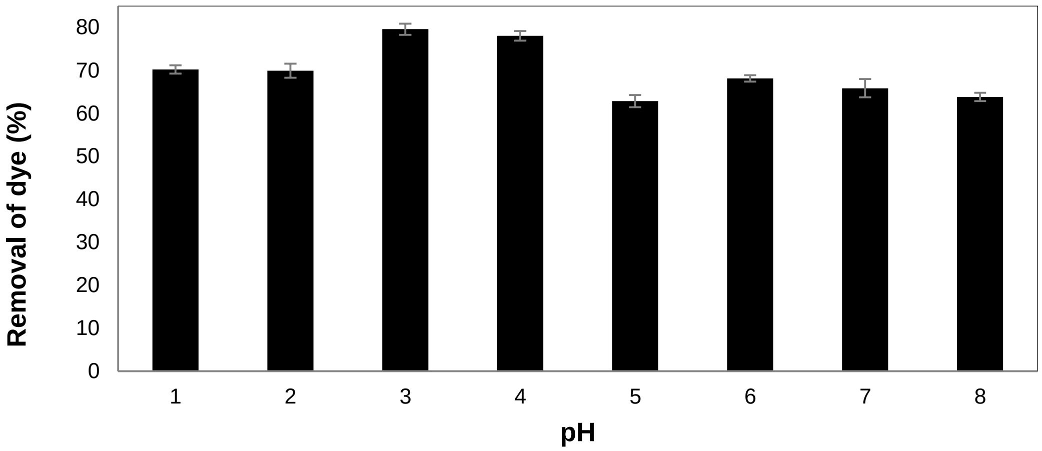


Fig. 7. Effect of initial pH on removal of RB5 by MPKS

Isotherm study

Adsorption isotherms show the relationship between the amount of adsorbate adsorbed per unit gram of adsorbent and the concentration of adsorbate in the bulk liquid phase once equilibrium has been reached. Three isotherm models, namely the Langmuir, Freundlich, and Redlich-Peterson models, were used to analyze the data. The isotherm parameters as listed in Table 5 were identified using a non-linear method. The sum of the square of errors function (ERRSQ) (Eq. 8) was used together with solver add-in in Microsoft's Excel spreadsheet to minimize the error function across the concentration range studied in order to determine the constants (Gimbert *et al.* 2008). A non-linear method was chosen over a linear method to eliminate the inherent bias resulting from linearization,

$$\text{ERRSQ} = \sum (qe_{calc} - qe_{exp})^2 \qquad (8)$$

where, qe_{exp} is adsorption capacity from the experiment and qe_{calc} is the adsorption capacity calculated by using isotherm models.

Table 5. Parameters of Isotherm Models for Adsorption of RB5 by MPKS

Isotherm models	Parameters				R^2
	K_L (L g^{-1})		α_L (L mg^{-1})	q_m (mg g^{-1})	
Langmuir	258.474		1.347	191.89	0.901
	K_F (L mg^{-1})	$1/n_F$			
Freundlich	117.770	0.088			0.854
	K_R (L g^{-1})	β	α_R (L mg^{-1})		
Redlich-Peterson	367.551	0.962	2.357		0.943

Figure 8 compares the isotherm models with experimental data. Generally, the Redlich-Peterson model yielded the best fit in describing adsorption of RB5 by MPKS over the entire concentration range by demonstrating the highest coefficient of determination, R^2, of 0.943. It can be concluded that the adsorption of RB5 by MPKS is best represented as a combination of both Langmuir and Freundlich isotherm models. At high concentrations, the adsorption of RB5 on MPKS approaches the Freundlich isotherm, whereas at low concentrations it approaches the Langmuir isotherm (Redlich and Peterson 1959). Therefore, at low dye concentrations, monolayer adsorption was observed, whereas at high concentrations, multilayer adsorption occurred. Furthermore, the Langmuir isotherm characteristic was found to be dominant in this adsorption system because the β value was near to 1. The value of q_m for adsorption of RB5 on MPKS predicted from Langmuir isotherm agreed with the experimental result, with values of 191.9 mg/L and 207.5 mg/L, respectively.

RB5 removal efficiencies as a function of time with various initial dye concentrations are shown in Fig. 9. The percentages of dye removal were 97%, 89%, 59%, 46%, 37%, 33%, 30%, and 26% for initial concentrations of 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L , 500 mg/L, 600 mg/L, 700 mg/L, and 800 mg/L, respectively. Low initial dye concentration exhibited higher removal percentage of RB5 by MPKS than high initial concentration. As initial concentration increases, the number of mole of the dye molecules increases; however the amount of active adsorption sites on the adsorbent is constant. Therefore, only a fixed amount of dye molecules were adsorbed on MPKS, resulting in lower adsorption efficiency as the dye initial concentration increases. Adsorption of RB5 on MPKS had reached approximately 70% or more after adsorption for a day (Fig.9), indicating that MPKS has high removal efficiency in terms of time.

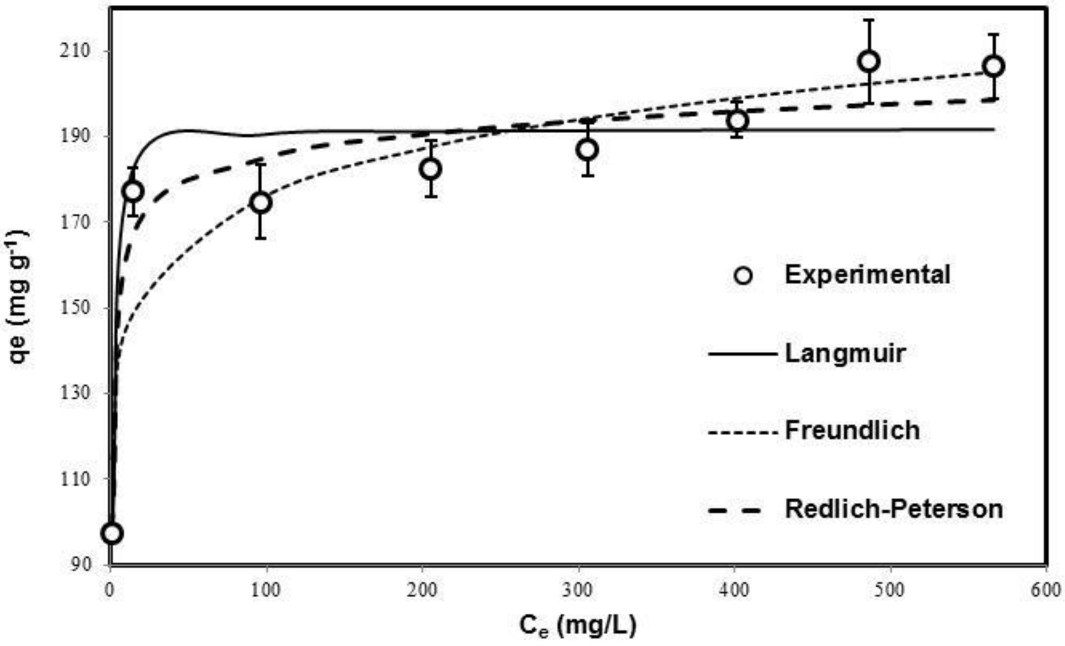


Fig. 8. Curve fitting of adsorption equilibrium data of RB5 by MPKS to Langmuir, Freundlich, and Redlich-Peterson isotherms

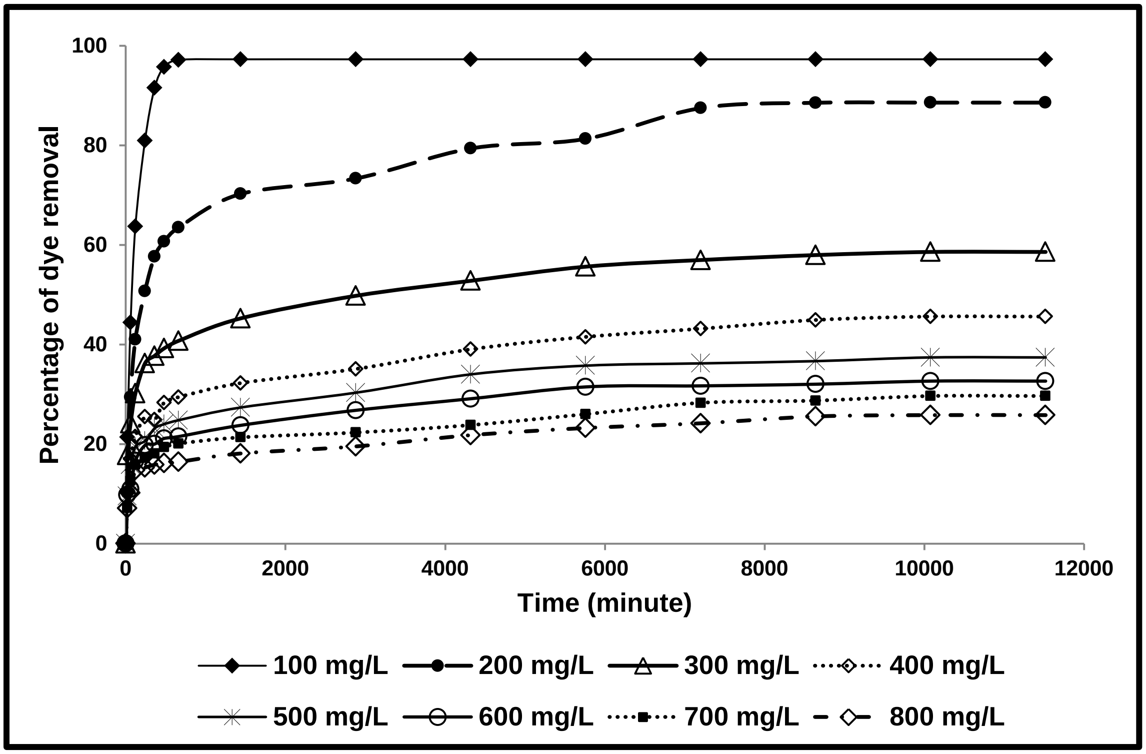


Fig. 9. RB5 removal efficiencies as a function of time with various initial dye concentrations from 100 mg/L to 800 mg/L

The chemically modified MPKS is a better adsorbent for RB5 removal when compared with activated carbon (AC) in terms of its maximum adsorption capacity (q_m). The q_m value for RB5 by MPKS was found to be 207.5 mg/g. Table 6 shows the comparison of q_m for adsorption of RB5 on MPKS and activated carbon. The MPKS particle size of 1 to 0.25 mm offers an extra advantage relative to other finer adsorbents, as filtration steps are needed for powdered adsorbent, and such operations are not cost and time effective. Thus, MPKS has advantages over activated carbon as adsorbent for removal of RB5 from aqueous solution in terms of both cost and efficiency.

Table 6. Maximum Adsorption Capacity (q_m) for Adsorption of RB5 on MPKS and Activated Carbon (AC)

Adsorbent	Particle size (mm)	q_m (mg/g)	References
Granular MPKS	1.0-0.25	207.5	This work
Palm kernel shell AC	1.7-0.6	81.34	Nourouzi *et al.* (2009)
Bamboo AC	2.0-1.0	39.02	Ahmad and Hameed *et al.* (2010)
Commercial AC		198	
Bamboo AC	0.35–0.18	286	Ip *et al.* (2010)
Bone char		160	
Sawdust-based AC	0.074	415.4	Vijayaraghavan *et al.* (2009)
Coal-based AC		150.8	

CONCLUSIONS

1. Quaternized granulated palm kernel shell (MPKS) was successfully produced and used as an adsorbent for removal of Reactive Black 5 dye (RB5).
2. The FTIR and CHN analyses confirmed that the quaternary ammonia group (NR_4^+) was present in the MPKS.
3. Granular MPKS exhibited an average pore diameter of 112.6 nm and surface area of 1.717 m^2/g.
4. pH 4 was the optimum pH for removal of RB5 on MPKS, as it presented the most positive surface charge.
5. The maximum adsorption capacity per unit mass of MPKS was 207.5 mg/g. The Redlich-Peterson isotherm was the best model in describing the adsorption process of RB5 by MPKS.

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