

Enhanced methylene blue removal from aqueous solution using modified rubber seed (*Hevea brasiliensis*)

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ABSTRACT

Nowadays, dyes have been considered as common industrial pollutants that are harmful to the environment. In order to address this problem, this study investigated the potential use of natural rubber (*Hevea brasiliensis*) seeds (NRS) to remove methylene blue (MB) from aqueous solution. NRS was pretreated using epichlorohydrin (ECH) and concentrated H₂SO₄ in various impregnation ratios to produce modified NRS called NRSEA. The structural and surface properties of the adsorbent were characterized using Fourier transform infrared and scanning electron microscope. The effects of different system variables (pH, initial MB concentration, contact time and adsorbent dosages) and the presence of ion intruders on adsorption capacity were studied. The results of MB adsorption ability test onto NRSEA showed that the adsorption capacity increased with increasing pH (within the pH range of 7–12) and decreased afterwards, the optimum initial MB concentration reached at 800 mg/L, and the equilibrium state was achieved at 120 min of contact time. Moreover, NRSEA was identified as having a higher adsorption affinity towards MB molecules than NRS. The isotherm data obtained from isotherm studies were fitted well to the Langmuir isotherm with a maximum adsorption capacity of 784.31 mg/g and best described by pseudo-second-order kinetic model. The thermodynamic test results exhibited that the adsorption process was endothermic and spontaneous at 45°C and 65°C.

Keywords: Cationic dye; Methylene blue removal; Adsorption; Rubber seed; Epichlorohydrin

1. Introduction

The rapid growth of various types of industries, such as textiles, paper, food processing, printing, plastics, cosmetics and synthetic dyes has triggered water pollution which needs to be seriously considered because of its adverse effects on living systems [1,2]. The harmful substances

contained in the waste can be acids, bases, organics, inorganics, heavy metals, dissolved solids and dyes. Among these pollutants, dyes are categorised into types of water pollutants which have the worst impact on health because of the fused aromatic ring and the conjugated chromophore in their structure [3]. The complexity of the molecular structure of these pollutants causes it to be difficult to degrade naturally.

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Moreover, water-soluble dyes can absorb more sunlight, consequently this will reduce the light penetration in the aquatic system and decrease the level of dissolved oxygen in the water [4–7].

Recently, dye in the world has reached more than 100,000 commercially available dyes with more than 7×10^5 tons of dyes produced annually. This massive use of dyes has resulted in an increase in the level of accumulation of these pollutants in the environment [8–10]. Moreover, it is currently estimated that approximately 30%–40% of these dyestuffs originated from industrial wastes are released into aquatic sewers [11]. Therefore, researchers need to work together to address these environmental problems for health and aesthetic reasons.

Dyes can be classified into three groups [12]: cationic (basic dyes), anionic (direct, acid and reactive dyes) and non-ionic (dispersive dyes). Methylene blue (MB) is a thiazine ($C_{16}H_{18}NSCl$) derivative compound, which is most commonly used in textile industry [13]. As a cationic dye, MB can interact with negatively charged cell membrane surface, enter into cell and accumulate in the cytoplasm. MB is also known as a basic dye with high solubility in water and is highly visible in water even at very low concentrations [14]. MB may even cause irritation to the skin and cause eye burns which can be responsible for permanent injury. It can also cause some harmful effects on human beings such as vomiting, increased heart rate, diarrhoea, convulsions, dyspnea, shock, cyanosis, jaundice, quadriplegia and tissue necrosis [15–17]. Hence, removal of MB efficiently from aqueous solutions is one of the important issues that must be considered.

Currently, numerous methods and technologies by physiochemical, biological or chemical processes to treat the problems are still being developed by scientists. However, each of these treatments still has its own limitations in terms of design simplicity, by-products generation, separation efficiency and initial costs [7]. For example, the advantage of the electrochemical method is to generate non-hazardous end products, but they still require high electricity costs. Physio-chemical processes such as membrane filtration have the advantage of removing all type of dyes depending on the pore size and thickness of the filter membrane, but have a disadvantage in clogging the membrane pores resulting in membrane fouling and leading to producing concentrated sludge [18,19].

Adsorption, which is a promising method in developing water treatment to remove MB, is a well-known method with low operating costs, simple design, and a high possibility for adsorbents to be recycled and reused [1,6,20,21]. In some previous studies, commercial activated carbon has been popularly used as an adsorbent due to its large surface area, micro-porous structure, high adsorption capacity and high surface reactivity. However, high cost of activated carbon has motivated researchers to find cheap materials mainly derived from local agriculture origin [22,23]. Consequently, a series of experiments are needed to find adsorbents with excellent properties for removing dyes from aqueous solutions.

Our work focused on evaluating the possibility of natural rubber (*Hevea brasiliensis*) seeds (NRS), one of the agricultural wastes, to be used as an adsorbent in the treatment

of industrial wastewater pollution. Natural rubber tree is one of the seed plants containing nonedible oil which has received much attention of researchers in recent times. This plant belongs to the family of Euphorbiaceae and is a member of the genus *Hevea* [24]. This tree originates from the Amazon region of Brazil but mainly grows in Southeast Asian countries, for example, Indonesia [25]. This plant is cultivated for the extraction of milky latex as the primary source of natural rubber. The second most valuable product after latex is NRS which is rich in fiber, sugar, fatty acids and protein [26–28]. Polar functional groups that exist in the molecular structure of the compounds contained in NRS can contribute to their interactions with polar organic molecules, for example with MB [26,29]. In order to enhance the rubber seeds resistance against chemicals as well as to improve their adsorption ability and mechanical strength, modification of functional groups in rubber seeds is a process that is absolutely necessary.

The aims of this study were to improve the performance of NRS as a cheap and efficient natural adsorbent by modifying it with epichlorohydrin (ECH), to investigate the optimum conditions in the adsorption process and determine the adsorption mechanism that occurs between the modified NRS and MB. ECH is a chlorinated epoxy compound used as an industrial solvent with molecular formula C_3H_5ClO . ECH is an electrophilic compound that is highly reactive and is used in the manufacture of epoxy resins, synthetic glycerin and elastomers [30]. Because of its highly active properties, ECH is widely used as a crosslinking agent to increase polymer reactivity as an adsorbent [31–33]. The high electrophilicity of ECH made it to be selected as a material to modify NRS in this study. With this modification, it is expected that the NRS adsorption ability of the cationic dyes (MB) will increase. In addition, until now, no study has been conducted to investigate the ability of NRS modified by ECH in removing dyes in aqueous solutions.

In this study, NRS was first modified by ECH with a different NRS and ECH mass ratio (which is subsequently named as NRSE). NRSE beads were then treated by concentrated H_2SO_4 (named as NRSEA). The adsorbents were characterized by Fourier transform infrared (FTIR) and scanning electron microscope (SEM) measurements. To determine the adsorbent with optimum properties, MB adsorption capacity to NRS, NRSE and NRSEA were compared, and then applied for further experiments. The effects of various parameters on MB removal, such as contact time, dye concentration, biosorbent dosages, pH and temperature were investigated to verify the adsorbent with the highest adsorption performance. Finally, the kinetic, thermodynamic and isotherm properties of MB removal using the resulted material were also investigated.

2. Materials and methods

2.1. Chemicals and reagents

The methylene blue (MB) used in this work was purchased from Sigma-Aldrich (Singapore). A stock MB solution was prepared by dissolving an appropriate portion of solid dye in the double distilled water to a certain volume. The desired concentration of the test solution was prepared

by diluting the stock solution. Epichlorohydrin (ECH), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), *n*-hexane (C_6H_{14}) and sodium hydroxide (NaOH) were purchased from Merck (USA). All chemicals used were of analytical grade and without further purification.

2.2. Adsorbent pre-preparation

The rubber seed used in this study was collected from a rubber estate in the Siak district in Riau Province, Indonesia. The seed was separated manually from a rubber fruit and then washed with distilled water. The washed seed was dried at 110°C for 24 h and then crushed using a FRITSCH pulverisette-25 grinder machine to produce the granular shape. After completing the grinding, the granule was soaked with *n*-hexane, stirred with a magnetic stirrer, settled for a night and then filtered to remove the oil resulted from the crushed seeds. The granule was then placed in an oven at 110°C for 24 h and crushed to produce rubber seed in powder form (named as NRS). Using a laboratory sieve, the fraction of 80 mesh-size NRS was separated and stored for further use.

2.3. Preparation of NRSE

In this modification step, an amount of 25 mg NRS was suspended in 0.01 M ECH solution to obtain NRS:ECH ratio of 1:2, 1:4, 1:6 and 1:8 (w/w). Each solution was stirred continuously using magnetic stirrer at 200 rpm for 5 h. After completing the stirring, the modified NRS (named as NRSE) was filtrated and washed by distilled water until no colour was detected in the filtrate. NRSE were then soaked by *n*-hexane for 1 h and then placed in an oven for 20 min at a temperature of 100°C. The dried NRSE was then crushed using a FRITSCH pulverisette-25 grinder machine and filtered to obtain 80 mesh-size NRSE powder. Adsorption study was performed using 25 mg adsorbent in 25 mL of 100 mg/L (w/v) MB solution for 120 min at 200 rpm and analyzed by an ultraviolet-visible spectrophotometer model UV-Vis 1601 (Shimadzu, Japan) at 664 nm.

2.4. Preparation of NRSEA

In order to activate NRSE by H_2SO_4 , a preliminary study was conducted to determine the optimum impregnation ratio of the adsorbent with H_2SO_4 . The study was carried out by impregnating 50 mg NRS in concentrated H_2SO_4 with impregnation ratio of 1:2, 1:4, 1:6 and 1:8 (w/w) at 85°C for 5 h. After completing the washing and drying steps, each of the activated NRS was then contacted with 200 mg/L (w/v) MB solution and measured by UV-Vis spectrophotometer. The selected impregnation ratio was then used for treating the selected NRSE (obtained from section 2.3) with concentrated H_2SO_4 at 85°C for 5 h. The suspension was then filtered and extensively rinsed with distilled water to remove the acid that may still remain on the solid phase. The washing process was repeated until the pH of washing solution reached 7.0. Finally, the material obtained (named as NRSEA) was placed in an oven for 2 h at the temperature of 110°C and crushed using a FRITSCH pulverisette-25 grinder machine to form NRSEA powder and filtered on an 80 mesh filter.

2.5. Adsorbent characterization

Analysis on the functional groups of NRS, NRSE and NRSEA that might be involved in MB adsorption was performed using Fourier transform infrared spectrophotometer (PerkinElmer FT-IR System 1600 Model) in the range of 400–4,000 cm^{-1} . Simultaneous thermogravimetric analysis with differential scanning calorimetry (TGA/DSC) was carried out using STA LINSEIS PT1600 apparatus from Germany. The surface morphology analysis of NRS, NRSE and NRSEA was performed using SEM analysis (Model Leica Cambridge S360) with 500x, 1,000x and 20,000x magnifications at 15 kV. SEM with energy dispersive X-ray spectroscopy (SEM-EDX) was conducted by using JEOL IT300 instrument with 800x magnification at 10 kV, (JEOL, Japan).

2.6. Batch adsorption experiments

A fixed amount of adsorbent (25 mg) was weighed into a set of each 50 mL erlenmeyer flasks containing 25 mL MB solutions in a thermostatic shaker bath (Innova 3000) at 200 rpm to elucidate the values of several test parameters including pH (7–13), contact time (0–120 min), initial dye concentration (100–1,000 mg/L) and adsorbent dosage (0.01–0.1 g). The pH of the suspension was adjusted by using 0.01 M NaOH and 0.01 M HCl solution. After all the removal experiments were completed, the samples were filtered using Whatman paper No.4 to separate the adsorbent from the dye solution. The residual dye molecules concentration in the solution was then analyzed by a UV-Vis spectrophotometer at 664 nm. The removal percentage (%) of MB was calculated using the following equation:

$$\text{Removal percentage} = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

where C_i and C_e are the initial and equilibrium concentration of MB in solution (mg/L), respectively.

The adsorption capacity of an adsorbent obtained from the mass balance on the adsorbate in a system with a volume of solution V , expressed as:

$$q_e = \frac{C_i - C_e}{m} \times V \quad (2)$$

where q_e is dye concentration at equilibrium onto adsorbent (mg/g), C_i and C_e are the initial and final concentration of MB in solution (mg/L), respectively. V is the volume of solution (L) and m is the mass of adsorbents (g) used. The optimum adsorbent was used for the next sorption experiments.

2.7. Adsorption isotherm studies

The isotherm properties of MB adsorption onto adsorbent were evaluated in order to establish the most appropriate correlations for the equilibrium data in the adsorption system. In general, this experiment was carried out with the same procedure as Section 2.6 by using 25 mg of adsorbent. The adsorption was performed at various MB concentrations of 200, 400, 600, 800 and 1,000 mg/L at pH 12. In this study, the experimental data were tested by Langmuir and

Freundlich models. The Langmuir isotherm theory assumes that maximum adsorption corresponds to a saturated monolayer of the solute molecule on the adsorbent surface. The Langmuir equation [34] is given as follows:

$$q_e = \frac{q_m \times b \times C_e}{1 + b \times C_e} \quad (3)$$

where q_e is dye concentration at equilibrium onto adsorbent (mg/g), C_e is dye concentration at equilibrium in solution (mg/L), q_m and b are the maximum adsorption capacity (mg/g) and Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption, respectively.

The Freundlich equation is an empirical equation employed to describe heterogeneous system, in which it is characterized by the heterogeneity factor $1/n$. The Freundlich equation [35] is written as follows:

$$q_e = K_f \times C_e^{\frac{1}{n}} \quad (4)$$

where C_e is dye concentration at equilibrium in solution (mg/L), q_e is dye concentration at equilibrium onto adsorbent (mg/g). K_f , $((\text{mg/g})/(\text{mg/L})^{1/n})$ and n are Freundlich constants. A value of $1/n$ is a measure of adsorption intensity or surface heterogeneity and ranging between 0 and 1.

2.8. Adsorption kinetics and thermodynamic studies

Adsorption kinetic experiments were carried out by agitating 25 mL of MB solution with a known initial dye concentration of 800 mg/L with 25 mg of NRSEA at pH 12 for several reaction times in the range of 5–120 min. At certain time intervals, the residual dye molecules concentration in the solution was similarly measured. The amount of adsorption at time t , q_t (mg/g), was calculated by using Eq. (5).

$$q_t = \frac{C_i - C_t}{m} \times V \quad (5)$$

The thermodynamic studies were also conducted with the same procedures and conditions as the adsorption kinetics procedure with various initial MB concentrations of 200, 400, 600, 800 and 1,000 mg/L under various temperatures of 25°C, 45°C and 65°C.

2.9. Effects of another ion presence

The effects of the presence of neutral red (NR) on the MB removal was investigated by adsorbing the dyes onto NRSEA with a mass of 25 mg adsorbent. In this study, MB concentration was maintained at 800 mg/L while the NR concentrations were added in the range of 0–500 mg/g into the solution and shaken in a thermostatic shaker bath for 120 min. After the reaction was finished, the sample was filtered using Whatman paper No. 4 to separate the adsorbent from the dye solution. The residual dye concentration in the solution was then analyzed by a UV-Vis spectrophotometer at 664 nm.

3. Results and discussion

3.1. Characterization of adsorbent

The surface physical morphology of NRS before and after the modification was observed by SEM technique. Fig. 1a shows the micrographs of NRS, NRSE and NRSEA at three different scales (500x, 1,000x and 20,000x magnifications). Through the picture, it is clear that the modification and activation of NRS changed its particle size and morphology. After modification, the adsorbent particle size turned out to be smaller than before. Moreover, the surface of NRSE is sharper and rougher than NRS. By using larger magnification (20,000x magnification), it can be seen that the adsorbent surface after activation with sulphuric acid becomes more flat and uniform. Such differences may have an effect on the adsorbent's ability to adsorb the dye. The adsorption capacity is increased as the particle size becomes smaller because it has a larger total surface area for adsorption [36]. Moreover, a rough and uniform surface of adsorbents will allow the dye to be adsorbed. To further investigate this, a series of characterization and adsorption test are conducted.

FTIR spectrum of the adsorbent was recorded to understand the mechanism of NRS modification by ECH and it is shown in Fig. 1b. From the spectrum of NRS, NRSE and NRSEA, some peaks were shifted or disappeared and some new peaks were also detected. The characteristic peaks

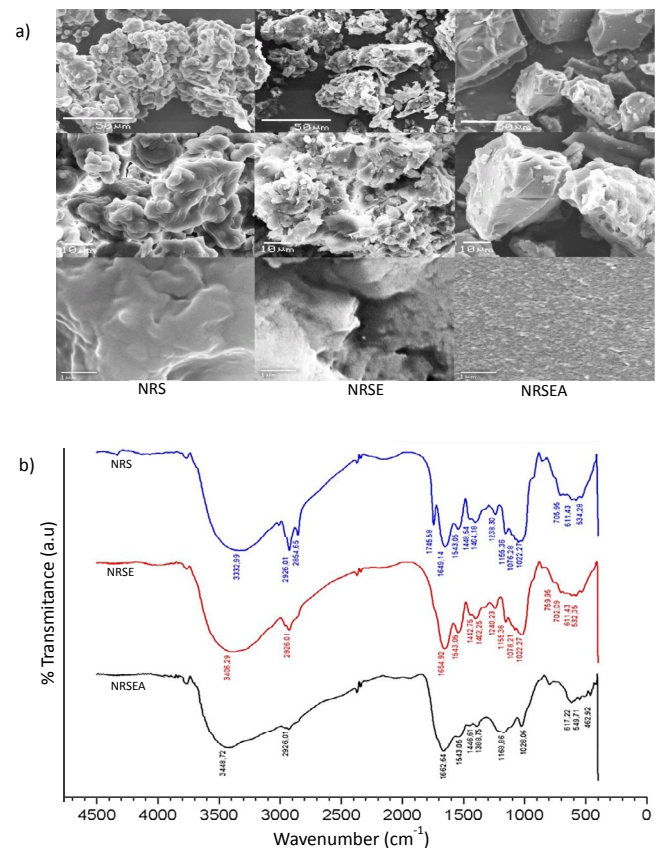


Fig. 1. (a) SEM micrograph of NRS, NRSE and NRSEA at 500x, 1,000x and 20,000x magnifications (from top to bottom, respectively) and (b) FTIR spectrum of the adsorbents.

appearing around 1,649–1,662, 2,926 and 3,300–3,448 cm^{-1} are due to C=O stretching on amide, C–H stretching on alkane and hydroxyl (–OH) stretching vibration, respectively. However, C=O carboxylic stretching at 1,745 cm^{-1} and –CH₂ stretching at 2,854 cm^{-1} are not observed on adsorption band of modified NRS which indicated that the carboxylic acid on NRS has been chemically attached to ECH. Comparing with NRSE spectrum, C–O stretching vibration at 1,238 cm^{-1} is not present on NRSEA spectrum. This indicates that the activation process onto modified NRS causes the change of functional groups on NRSE which ultimately resulted in a peak shift on NRSEA spectrum.

SEM-EDS analysis was conducted to compare the chemical composition of adsorbent before and after modification/activation. From the results, the type of interaction between NRS and the modifying agents can be predicted leading to knowing functional groups that play an important role in the adsorption process. Compared with NRS and NRSE, the micrograph of NRSEA surface is more heterogeneous, not only containing carbon (C) and oxygen (O), but also nitrogen (N) and chlorine (Cl) (atomic abundance is more than 1%) as a result of the interactions between NRSE and ECH. From Fig. 2b, there are no N and Cl found on the NRSE surface (NRS modified without activation by concentrated H₂SO₄),

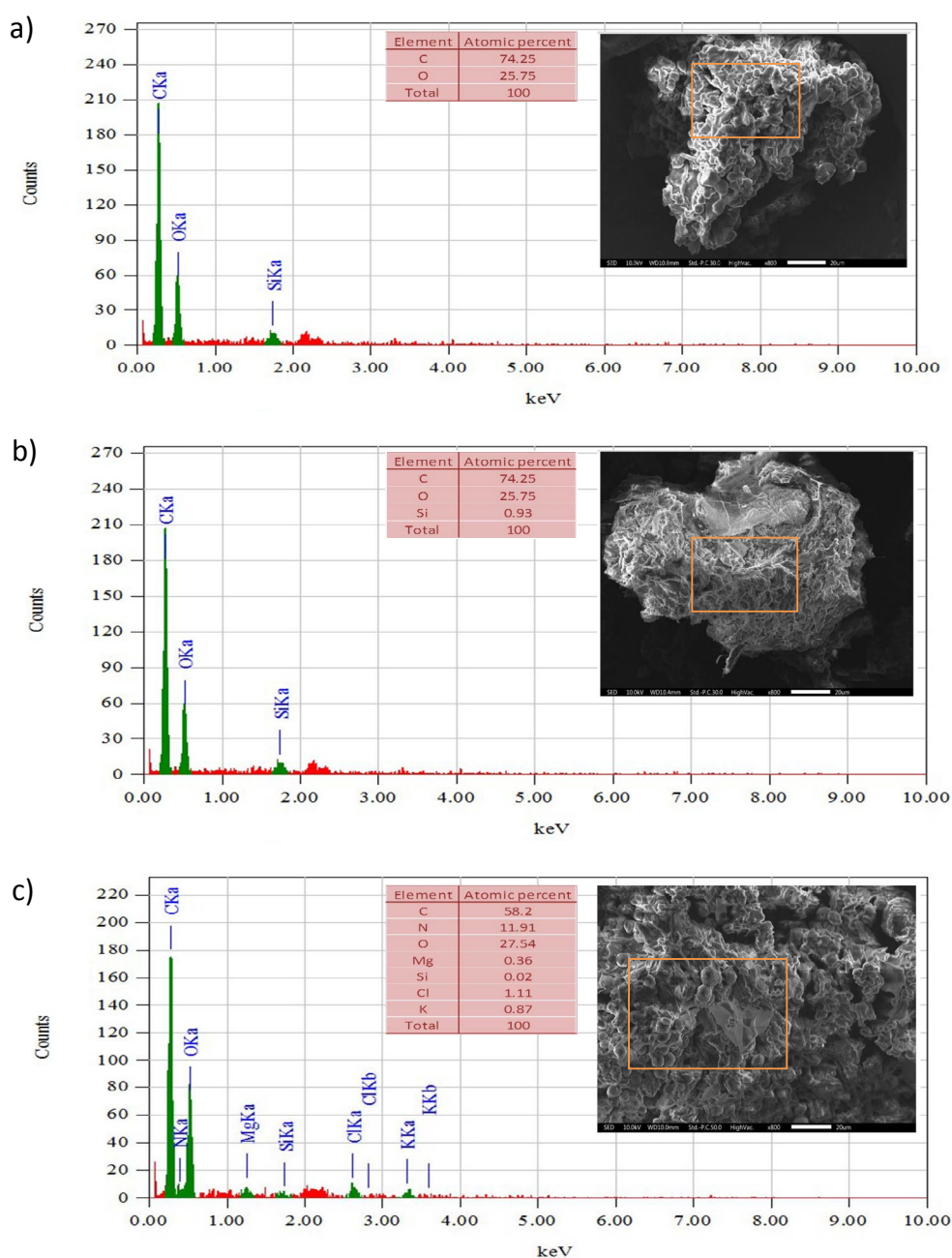


Fig. 2. SEM-EDX analysis of (a) NRS, (b) NRSE and (c) NRSEA.

indicating that ECH physically interacts onto NRS surface which results in leaching out during the washing process. Thus, it can be concluded that activation of NRS is a crucial step to generate chemical interactions between NRS and ECH which played as active sites in MB adsorption. This activation can also induce the cross-linking reaction between the acid and modified NRS on the carbon structure [37], denaturation of proteins and hydrolysis of carbohydrate and fibres which are contained in the rubber seeds [38]. Hydroxyl and carboxyl groups that are generated from those reactions may be acted as active groups on the adsorption process. In the other words, activation of modified NRS by sulphuric acid can increase the adsorption capacity.

The TGA thermograms of NRS, NRSE and NRSEA are shown in Fig. 3. From the figure, there are three main degradation steps which represent the rubber seed contents. Water content is represented by the first slope (50°C–100°C) while volatile compounds are represented by the second slope (100°C–200°C) and the fixed carbon is represented by the third slope (200°C–400°C) [39]. The thermograms show that the temperature range for all degradation steps of NRSE is always higher than NRS indicating that the modification by ECH can increase the thermal stability of the adsorbent. However, NRSEA shows lower thermal stability than NRSE and slightly higher than NRS due to the new linkages (physical interactions and chemical bonds) formed between NRS activated by H_2SO_4 and ECH. Generally, the TGA results showed that the thermal stability of the rubber seed-based adsorbent increased but did not change significantly by modification with ECH and activation using concentrated H_2SO_4 .

3.2. Sorption studies

3.2.1. Effect of impregnation ratio

The influence of impregnation ratios between the prepared NRS with ECH and concentrated H_2SO_4 was analyzed using Eq. (1) and the results are shown in Fig. 4. The curve represents that the percentage of MB removal can achieve an optimum value at NRS:ECH impregnation ratio

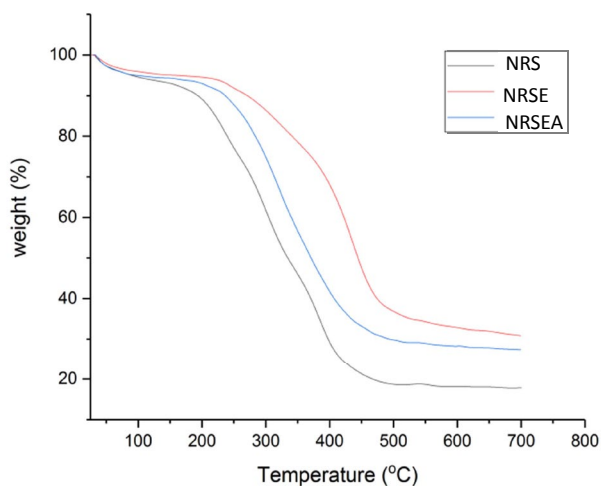


Fig. 3. Thermogravimetric analysis of NRS, NRSE and NRSEA.

of 1:6. Impregnation of NRS with sulphuric acid also shows the same optimum impregnation ratio, that is, 1:6 (w/w). Therefore, this ratio was chosen for the modification of NRS and activation of NRSE.

3.2.2. Effect of adsorbent modification

The adsorption study of NRS, NRSE and NRSEA was carried out to identify the adsorbent with the highest adsorption rate. By knowing the initial and final concentrations of the MB solution, the adsorbent capacity can be calculated by using Eq. (2) and the results are shown in Fig. 5. The curve represents that the amount of dye adsorbed (mg/g) increases by increasing the time of adsorption process and tends to constant after equilibrium time. Moreover, modification by ECH increases the q_e value of the rubber seed. NRSEA is identified as the highest adsorption capacity and used in the subsequent adsorption test.

3.2.3. Effect of initial dye concentration

The adsorption capacity in an adsorption process is correlated to the dye concentrations. The effect of initial concentration on the MB removal by NRSEA is shown in Fig. 6a. The experiment was performed by stirring 25 mg of NRSEA and MB solution in the concentration range of 100–1,000 mg/L at pH 12 with a stirring speed of 200 rpm for 120 min. From Fig. 6a, the equilibrium adsorption capacity of NRSEA significantly increases from 98.7 to 729.5 mg/g as MB concentration increases from 100 to 800 mg/L. This is due to the increasing driving force for mass transfer along with the increase in MB concentration. However, after reaching 800 mg/L, a further increase in the MB concentration shows no significant change in the removal efficiency. The possible reason is that the excessive density of MB molecules in the solution has triggered the molecules to face tighter competition to interact with the adsorbent surface which leads to the limited active sites of the adsorbent that can be occupied by the adsorbates [40,41].

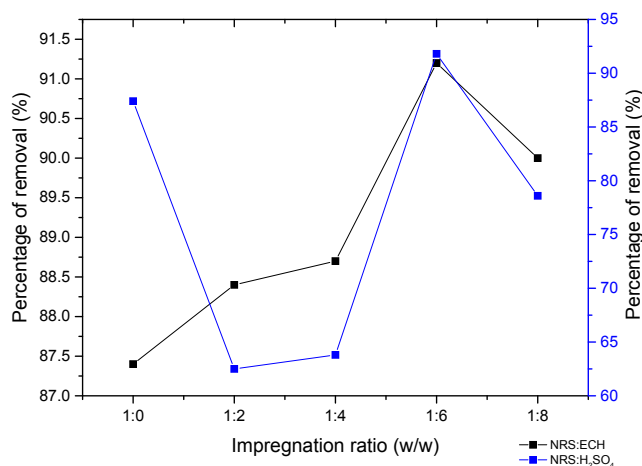


Fig. 4. MB removal curve of NRS by varying impregnation ratio. Conditions: $W_{\text{adsorbent}} = 25$ mg; $V_{\text{solution}} = 25$ mL; 100 mg/L MB solution; 120 min; 200 rpm shaking speed.

3.2.4. Effect of contact time

In order to determine the equilibrium time as a key factor in the MB removal by NRSEA, the effect of contact time was analysed at 800 mg/L of initial MB concentration using 25 mg NRSEA at pH 12 with stirring speed of 200 rpm for 2 h. As shown in Fig. 6b, for the first 90 min, it clearly shows that the amount of dye adsorbed increased linearly with the increase in contact time, however beyond that contact time, it gradually approached a value that is more or less constant,

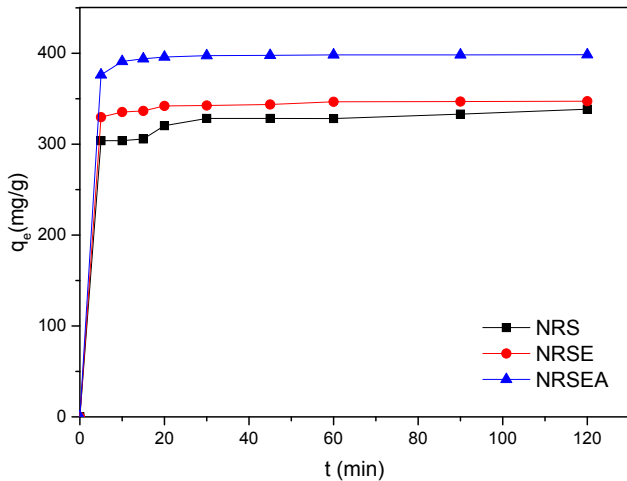


Fig. 5. Adsorption curve of NRS, NRSE and NRSEA by varying time in range of 0–120 min. Conditions: $W_{\text{adsorbent}} = 25$ mg; $V_{\text{solution}} = 25$ mL; 400 mg/L MB solution; pH 12; 120 min; 200 rpm shaking speed.

indicating the achievement of equilibrium. This adsorption rate can be associated with the availability of active sites on the adsorbent surface [42]. After the adsorbent surface is saturated enough, the system reaches a steady state leading to decreased MB adsorption rates identified from 90 to 120 min. In this study, 120 min of contact time was sufficient to achieve saturation in MB adsorption onto NRSEA.

3.2.5. Effect of pH

The adsorption capacity of an adsorbent is strongly influenced by pH. The functional groups (such as amino, carboxyl, thiol, sulfhydryl and phosphate) that are present on the adsorbent surface contribute to the equilibrium state in the adsorption process [43–45]. An activated adsorbent has a certain pH which is charged 0 and it is called as pH_{PZC} (point of zero charges). Based on previous report, pH_{PZC} of rubber seeds was found at pH 5.2 [46]. At pH values below 5.2, the NRS surface is positively charged and would be prone to electrostatically repelling cationic adsorbate. On the contrary, the NRS charge will be negative above this pH because of deprotonation of several polar functional groups of compounds contained in the rubber seeds [46–48].

As the cationic dye, MB has an overall positive charge which would give some contributions to the interaction between MB and the active site of adsorbent. Therefore, it is necessary to find the optimum pH of adsorption for the accuracy of the data. In this study, the influence of pH on the MB removal by NRSEA was investigated by adjusting pH in the range of 7 to 13 by adding 0.01 M NaOH or HCl solutions with 200 mg/L initial MB concentration and an amount of NRSEA (25 mg) at 200 rpm agitation speed.

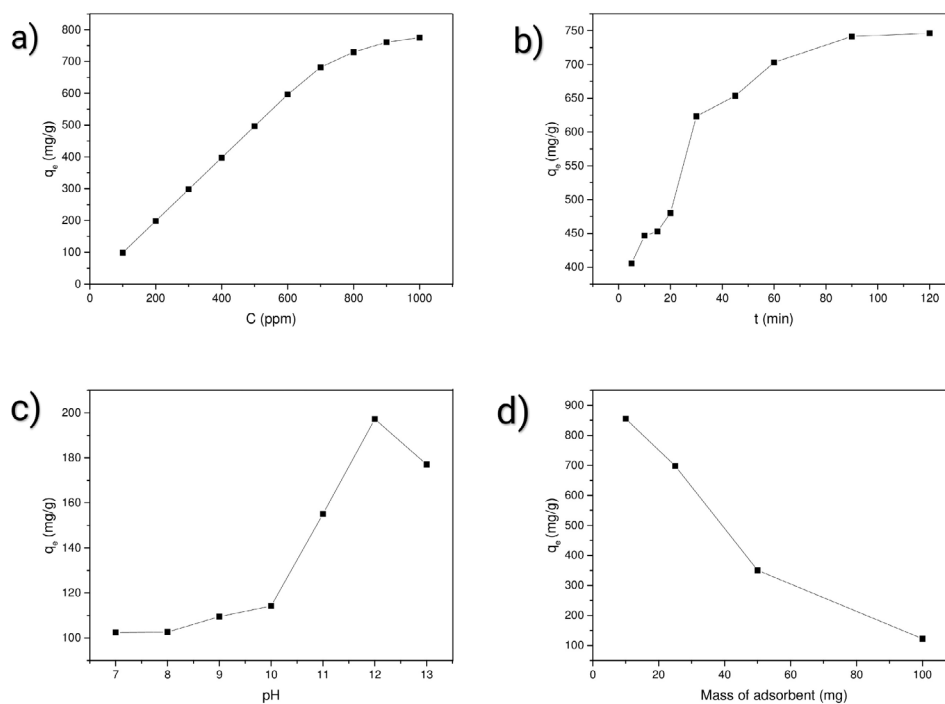


Fig. 6. Effect of several parameters on the MB removal by NRSEA, (a) MB initial concentration, (b) contacting time, (c) pH, (d) adsorbent dosage. Conditions: $W_{\text{adsorbent}} = 25$ mg; $V_{\text{solution}} = 25$ mL; 200 rpm shaking speed.

The effect of initial pH on the removal of MB can be seen in Fig. 6c. The curve shows that the amount of dye adsorbed increased from pH 7 to 12 and tended to decrease afterwards. At higher pH, the adsorbent will be negatively charged and preferably by the cationic adsorbate. However, at pH 13, the presence of hydroxyl ions in the solution becomes too much which results in reducing the solubility of MB. According to the result, pH 12 was chosen as the optimum pH for further experiments in this study.

3.2.6. Effect of adsorbent dosage

The amount of MB molecules that can be adsorbed onto NRSEA depends on the adsorbent dosage used. The effect of NRSEA dosage was studied by changing the quantity of NRSEA (10, 25, 50 and 100 mg) in each test solution while maintaining the initial dye concentration (800 mg/L) and pH 12 constant at 200 rpm for 2 h. Fig. 6d shows that q_e decreases with increasing mass of NRSEA. Adding a number of NRSEA dosages after 10 mg did not show a significant increase in MB adsorption. This can be caused by an increase in the amount of adsorbent which is not facilitated by increasing the amount of adsorbate in the solution [45]. Therefore, from this experiment, q_{max} was reached at 10 mg NRSEA with an adsorption capacity of 855.2 mg/g.

A different trend occurred when the analysis was done by calculating the percentage of MB removal. The percentage of MB adsorption onto NRSEA with adsorbent dosages of 10, 25, 50 and 100 mg were 42.76%, 87.28%, 87.59% and 61.28%, respectively. According to the results, the percentage of MB removal increased with an increase in adsorbent dosage due to the increasing number of active sites which could accommodate MB adsorption. The decrease in adsorption capacity along with the increase in the number of adsorbents is associated with the presence of unsaturated active sites available on the surface of NRSEA during MB adsorption [48]. From this experiment, further experiments were carried out using 25 mg of NRSEA because there was no significant increase in the MB removal percentage observed for dosage above 25 mg due to the sufficient active sites available to adsorb MB molecules from the aqueous solution.

3.3. Adsorption isotherm study

The study adsorption isotherm needs to be investigated to provide an explanation of how the adsorbent will interact with the adsorbate. It also has an important role in understanding the mechanism of adsorption [49]. The adsorption capacity of NRSEA for MB removal was evaluated using the two common isotherm models (Langmuir and Freundlich adsorption isotherm). Langmuir isotherm refers to homogeneous adsorption, where adsorption can occur on a number of certain local sites, without the migration of adsorbates in the surface plane [34]. Contrary to that, the Freundlich model is applicable to multilayer adsorption on heterogeneous surfaces [35].

Based on the analysis using Eq. (3), Langmuir adsorption isotherm curve is obtained by plotting C_e/q_e to C_e as seen on Fig. 7a. On the other hand, Freundlich adsorption isotherm analysis was conducted using Eq. (4) and the result is shown in Fig. 7b. The Langmuir and Freundlich parameters,

along with R^2 values are presented in Table 1. Where q_e is dye concentration at equilibrium onto adsorbent (mg/g), C_e is dye concentration at equilibrium in solution (mg/L), and q_m (mg/g) and K_L (L/mg) are Langmuir constants which are related to maximum adsorption (monolayer) capacity and energy of adsorption, respectively. These constants were measured from the linear plot of C_e/q_e vs. C_e (that is illustrated in Fig. 7a) with $1/q_m$ as a slope and $1/q_m K_L$ as an intercept. Based on those two adsorption isotherm curves, the coefficient of determination (R^2) of the linear plot from Langmuir isotherm curve is greater ($R^2 = 0.9996$) than R^2 value of Freundlich isotherm curve ($R^2 = 0.597$). By comparing the correlation coefficient R^2 , it can be deduced that the experimental equilibrium adsorption data are well described by the Langmuir isotherm model than the Freundlich isotherm model. This indicates that there was monolayer coverage of the NRSEA surface by MB molecules. Based on the Langmuir adsorption isotherm model, the maximum adsorption capacity of MB onto NRSEA from the aqueous solution was found at 784.31 mg/g.

3.4. Dye adsorption kinetic studies

Adsorption kinetic parameters are important to investigate to predict the rate of MB adsorption onto NRSEA and provide data values to understand the adsorption mechanism. The study of MB adsorption kinetics was performed by varying the equilibrium times in the range of 1–120 min. Pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the best model fitted with MB

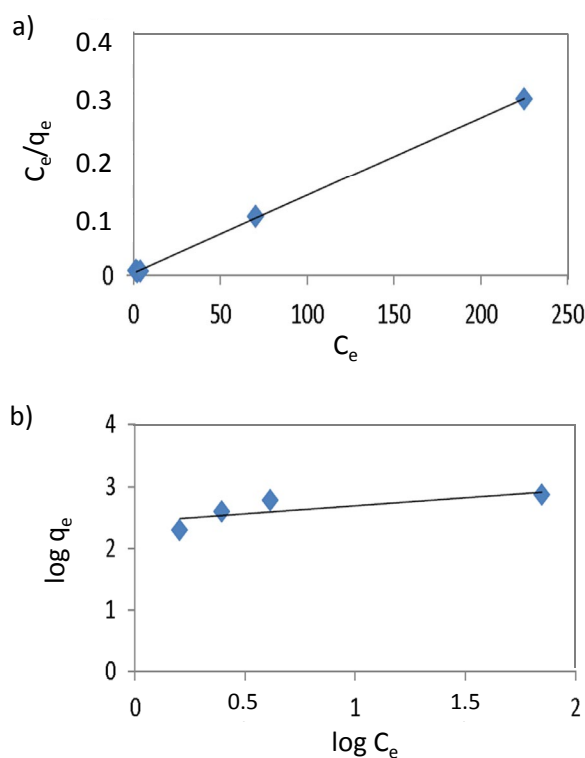


Fig. 7. (a) Langmuir and (b) Freundlich adsorption isotherm curves. Conditions: $W_{adsorbent} = 25$ mg; $V_{solution} = 25$ mL; pH 12; 200–1,000 mg/L MB solution.

Table 1
Adsorption isotherm parameters on MB removal by NRSEA

T (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	$1/n$	$K_F((\text{mg/g})/(\text{mg/L})^{1/n})$	R^2
298	784.314	0.305	0.9997	0.2601	272.019	0.597

adsorption by NRSEA. Pseudo-first-order kinetic equation was first proposed by Lagergren as follows [50]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (6)$$

where q_e is dye concentration at equilibrium onto adsorbent (mg/g), q_t is dye concentration at any time onto adsorbent (mg/g), k_1 (min^{-1}) was determined from the plot of $\log(q_e - q_t)$ against t (Fig. 8a).

In many cases, Lagergren's first-order equation does not match the entire time range of contact and is generally applicable during the initial stage of the adsorption processes [51]. Therefore, the pseudo-second-order kinetic models were also evaluated in this experiment. Eq. (7) was used to determine the pseudo-second-order kinetic parameters.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad (7)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the second order rate constant. The k_2 and q_e were generated from the slope and intercept of the plot t/q_t against t (Fig. 8b).

Figs. 8a and 8b show that the linearity of the pseudo-second-order kinetics plot is better than the pseudo-first-order model. The parameters of those kinetic models are summarized in Table 2.

From Table 2, the R^2 values of the pseudo-second-order kinetic plots were found to be in the range of 0.9961 to 0.9998. Moreover, the difference between the calculated q_e and the experimental q_e from pseudo-second-order kinetic model was closer than another model. The closeness between some parameters of the pseudo-second-order kinetic model and the theoretical data confirms that the MB removal kinetic by NRSEA is well represented by the pseudo-second-order kinetic model.

For the further steps, the kinetic results were measured by the intraparticles diffusion model to evaluate the diffusion mechanism. The calculation was carried out using Eq. (8) as follows [52]:

$$q_t = k_d t^{1/2} + C \quad (8)$$

where k_d is the coefficient of intraparticle diffusion rate ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C (gives an idea about the boundary layer thickness) is the intercept which can be determined from the

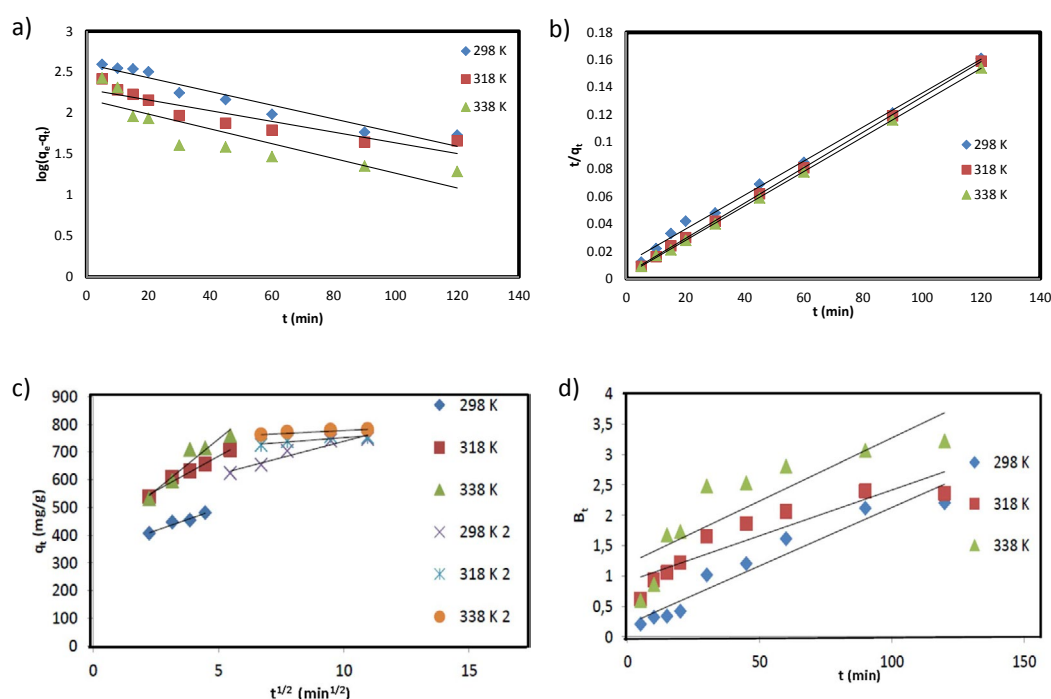


Fig. 8. (a) Pseudo-first-order adsorption curve; (b) pseudo-second-order adsorption curve; (c) intraparticle diffusion plot and (d) Boyd plot for MB removal by NRSEA. Conditions: $W_{\text{adsorbent}} = 25 \text{ mg}$; $V_{\text{solution}} = 25 \text{ mL}$; pH 12; 800 mg/L MB solution.

Table 2
Adsorption kinetic parameters of MB removal by NRSEA

T (K)	Pseudo-first-order			Pseudo-second-order			$q_{e,exp}$ (mg/g)
	q_{e1} (mg/g)	k_1 (min ⁻¹)	R_1^2	q_{e2} (mg/g)	k_2 (g mg ⁻¹ min ⁻¹)	R_2^2	
298	397.192	0.0193	0.9328	833.333	1.3×10^{-4}	0.9961	800
318	195.704	0.015	0.8439	769.231	4.5×10^{-4}	0.9998	
338	147.096	0.0207	0.7506	769.239	5.8×10^{-4}	0.9998	

plot of q_t against $t^{1/2}$ (Fig. 8c). If the intraparticle diffusion mechanism occurs, then the regression of q_t against $t^{1/2}$ will be linear. The rate-limiting process because of intraparticle diffusion only occurs if the plot passes the origin. Otherwise, it means some other mechanisms along with intraparticle diffusion are also involved [53]. From the plot, the first linear region corresponds to instantaneous adsorption stage (k_{d1}) related to the film diffusion. The second linear region (k_{d2}) is a gradual stage of adsorption where intraparticle diffusion is the rate limiting. Based on the curve, the plots were not linear over the whole time range and the second stage linear line did not pass through the origin. This emphasizes that intraparticle diffusion is not the only rate-limiting mechanism in the adsorption process [46,47,53]. The values of k_{d1} , k_{d2} , C_1 and C_2 as generated from the two straight lines are listed in Table 3.

Referring to Table 3, the thickness of the boundary layer (C) was found to be generally increased with the increasing temperature. This suggests that the diffusion effect on the formation of the boundary layer preferably occurs at higher temperatures because of the larger random motions associated with heat energy. Moreover, C_2 values are larger than C_1 and consequently the values of the intraparticle diffusion rates k_{d2} are smaller than the film diffusion rates k_{d1} . This gives a prediction that the process of dye adsorption can be controlled by intraparticle diffusion [54].

In order to determine the actual processes occurring in the MB adsorption process, the kinetic data obtained were further analyzed using the Boyd model which is calculated as follows [55]:

$$B_t = -0.4977 - \ln(1 - F) \quad (9)$$

F shows the fraction of adsorbate adsorbed at a given time which is given as follows:

$$F = \frac{q_t}{q_a} \quad (10)$$

Table 3
Intraparticle diffusion parameters of MB removal by NRSEA

T (K)	First linear region			Second linear region		
	k_{d1} (mg g ⁻¹ min ^{-1/2})	C_1	R_1^2	k_{d2} (mg g ⁻¹ min ^{-1/2})	C_2	R_2^2
298	31.306	338.95	0.9543	23.839	501.04	0.9241
318	49.756	436.47	0.9808	7.2403	679.88	0.8536
338	73.347	379.60	0.9172	4.3698	734.34	0.9272

where q_a shows the amount of dye adsorbed at infinite time (in this experiment = 120 min). The linearity of the calculated B_t vs. time t (min) can be used to identify the model of the adsorption process that occurs. From Fig. 8d, it can be seen that the Boyd linear plots at 318 and 338 K have a low correlation coefficient (lower than 0.90) indicating that the adsorption process was not dominated by intraparticle diffusion at both temperatures [53]. Contrarily, intraparticle diffusion mechanism was mainly occurred on MB removal by NRSEA at 298 K with a high correlation coefficient (higher than 0.90).

3.5. Thermodynamic study

The thermodynamic parameters that are considered to determine the adsorption process in this experiment were the changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The enthalpy change (ΔH°) and entropy change (ΔS°) of the adsorption were calculated using the van't Hoff equation as below [56].

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where K_d is the thermodynamic equilibrium constant and equal to q_t/C_e (L/mg), R is the universal gas constant (8.314 J/mol K) and T is the absolute solution temperature (K). From the calculated values of ΔH° and ΔS° , the Gibbs free energy change ΔG° can be calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The plot of $\ln K_d$ vs. $1/T$ was found to be linear and the thermodynamic parameters for the adsorption process were obtained and listed in Table 4. Based on the thermodynamic parameters in Table 4, the positive value of enthalpy change, ΔH° , suggests the endothermic nature of MB adsorption by NRSEA. Meanwhile, the positive value of entropy change,

ΔS° , indicates an increase in irregularities in the system due to increase in disorder of solid–liquid interface during the adsorption process. The Gibbs free energy change (ΔG°) shows the degree of the spontaneity of the adsorption process. In order to form a strong interaction between adsorbate molecules and the adsorbents, the value of ΔG° must be negative. In this experiment, ΔG° was positive at 298 K which indicated that the adsorption process was not spontaneous at room temperature. Further, the decreasing value of ΔG° with the increase in temperature indicates that the MB adsorption process by NRSEA is more favourable at high temperatures and spontaneously occurs at 45°C and 65°C.

Another thermodynamic parameter determined in this study was the activation energy (E_a). In the adsorption separation, E_a is defined as the minimum energy that the adsorbate must overcome to interact with the functional group on the surface of the adsorbent [57]. The activation energy of the adsorption process can be calculated using the Arrhenius equation [58]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (13)$$

where k is the rate constant of the pseudo-second-order kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$), E_a is the activation energy (kJ/mol), A is the Arrhenius factor, R is the universal gas constant (8.314 J/mol K) and T is the absolute solution temperature (K). E_a value also can explain the mechanism of adsorption. Physical adsorption generally has an activation energy of no more than 4.2 kJ/mol because the interactions involved are relatively weak. In contrast, chemisorption is specific and involves stronger interactions between the adsorbate and the adsorbent surface (E_a ranges between 8.4 and 83.7 kJ/mol) [59]. The activation energy obtained in this study was 32.634 kJ/mol (Table 4), which indicates that MB is chemically adsorbed onto NRSEA.

Several previous publications have shown the potential of some low-cost adsorbents to remove MB from aqueous solution and show similar trends in terms of adsorption mechanism, kinetics and thermodynamics with this study [13,22,60–64]. Table 5 summarizes the adsorption capacity of different type of adsorbents in MB removal. From these results, the adsorption capacity of each adsorbent varies and depends on the surface modification level of adsorbent and initial concentration of the adsorbate [65], as well as molecular size of the adsorbate and ionization rate per unit weight of the adsorbate [66], also the surface and affinity properties of each adsorbent [67]. These results showed that rubber seeds show promising potential in MB adsorption when compared with other biosorbents, mainly because of their low cost and easily obtained from nature.

3.6. Effect of another ion presence

The effectiveness of MB removal by NRSEA can be identified by investigating the effect of presence of other cationic dyes in aqueous solution on the adsorption process. Neutral red (NR) was used in this experiment as an intruder ion and added to the solution in the range of 0–500 mg/L while the MB concentration was maintained at 800 mg/L. According to the result, MB adsorption capacity with the presence of NR in the solution tends to decrease with the increase in NR concentration due to the competition between two positively charged ions to be adsorbed onto NRSEA surface. The negatively charged nature of NRSEA attracted not only MB molecules but also other cationic dyes such as NR. The decrease of removal percentage in the presence of the intruder ion reached a value of 17.57% after adding 500 mg/L NR to the solution. From this experiment, it can be concluded that the presence of other ions with the same charge as the adsorbate can reduce the adsorption capacity of the adsorbent.

Table 4
Adsorption thermodynamic parameters of MB removal by NRSEA

T (K)	K_L (L/mg)	K_d ($\text{mg g}^{-1} \text{min}^{-1/2}$)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)	E_a (kJ/mol)
298	0.305	0.712	0.779			
318	0.147	1.744	−1.324	32.118	105.164	32.634
338	0.153	3.289	−3.427			

Table 5
Comparison of adsorption capacity of various adsorbents in MB removal

Adsorbent	q_m (mg/g)	References
Activated carbon prepared from rattan sawdust	294.14	13
Carbon developed from <i>Ficus carica</i> bast	47.62	22
Fly ash–based geopolymer	37.04	60
Bamboo-based activated carbon	454.2	61
Rice husk	40.58	62
Rejected tea	147	63
<i>Posidonia oceanica</i> (L.) fibres	4.91	64
Rubber seed	784.31	This study

4. Conclusions

In this present study, according to the results of the characterisation of adsorbents, the modified and activated natural rubber seed, called as NRSEA, was successfully synthesised as an adsorbent to remove methylene blue (MB) from aqueous solution. NRSEA was identified to have the highest adsorption capacity among other adsorbents based on the studies of the effect of modifying the adsorbent. The capacity of MB adsorption onto NRSEA increased with the increase in pH (within the pH range of 7–12) and decreased afterwards, it also increased in the range of initial MB concentration from 100 to 800 mg/L, achieved a maximum percentage of MB adsorption at 25 mg of adsorbent, and reached a state of equilibrium after 120 min of contact time. The adsorption process was found to follow Langmuir isotherm model with a maximum adsorption capacity of 784.31 mg/g and the pseudo-second-order kinetic model. The calculated thermodynamic parameters indicated that the adsorption process was endothermic and spontaneous at 45°C and 65°C. Adsorption mechanism was found to be chemisorption and was dominated by intraparticle diffusion at room temperature. The presence of intruder ions such as NR can reduce NRSEA adsorption capacity.

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