Mangosteen Peel-Alginate Biocomposite Beads An Efficient and Sustainable Adsorbent For Decontamination of Methylene Blue

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Mangosteen peel-alginate biocomposite beads an efficient and sustainable adsorbent for decontamination of methylene blue

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Abstract

This study examines mangosteen peels waste and alginate beads (MPAB) as an efficient, sustainable and low-cost adsorbent for removal of methylene blue (MB) cationic dye from aqueous solution in a batch adsorption system. Surface functional groups, surface morphology, surface properties, and thermal stability of MBAB were analyzed using various instrumental techniques such as FTIR, FESEM, BET and TGA techniques. MPAB adsorption efficiency for MB was investigated through variation of dosage (0.01- 0.08g), pH (2- 10), contact time (60-1320 min), MB concentration (20- 100 mg/L) and temperature (298- 333K). MPAB showed maximum removal capacity of 373 mg/g at 25 ^{o}C in basic medium. Kinetic and isotherm studies showed that pseudo second order kinetic models and both Freundlich and Langmuir isotherms best fit the experimental data. The findings revealed that novel MPAB has the potential to be a cost-effective adsorbent for removal of textile dyes.

Keywords: Mangosteen peel waste; methylene blue; kinetic study; alginate beads; isotherm study

1. Introduction

In this modern day and age, novel dyes treatment technologies are required which can remove dyes from wastewater as well as reduce the potential toxicity to humans and the ecosystem [1]. Various types of technologies such as adsorption, membrane separation, coagulation, electrochemical , biological and adsorption are frequently used for wastewater containing dyes [2]. Among the various available method, adsorption is frequently used for decolorization of dye-containing water because of adsorption's economic and efficacious, and advantages. Different types of adsorbents such as activated carbon [3], geopolymer [4], clay minerals [5], industrial and agricultural wastes [6], zeolites [7] can be efficiently utilized in an adsorption process. However, these adsorbents have some disadvantages such as poor adsorption capacity and high cost [8].

Low-cost adsorbents require that the precursor be non-hazardous, easily accessible and relatively cheap. Much attention and interest have been increasing in using attractive, cheaper alternatives for decolorizing dye-contaminated water. In general, an adsorbent can be assumed to be "low cost" if it is freely available, requires little processing (such as by being a by-product), or is an industrial waste material that has lost its economic or further processing values. Indeed, the use of free biomass (industrial waste product or agricultural waste material) for the treatment of dyes through adsorption is a successful method. Biomass powder can effectively adsorb dyes due to high surface area; However, due to weak mechanical properties, low rigidity, high steric hindrance, high packing density and hydraulic conductivity, the powder form is not considered appropriate for column-type filtration [9]. Moreover, the powder biomass adsorbents are not easily recyclable and reusable. Due to the above mentioned disadvantages, the extensive use of powdered biomass or other agricultural adsorbents becomes narrowed due to process engineering difficulties such as reactor clogging, dispersion, and cost of regeneration [10, 11].

An alternate way exists to entrap the powder adsorbent in other supporting material, resulting in a new class of adsorbent. The utilization of alginate as a carrier substance for powdered adsorbent allows for the possibility of selective adsorption of dye molecules, depending upon the carrier charge, which interact with negative charge of carboxylate groups on alginate. Alginate is most commonly used because of its low cost, biodegradation, and ability to readily transform into hydrogels in aqueous solution [12]. Researchers have previously used Ca-alginate based adsorbent beads successfully to adsorb MB dye from aqueous solution [12-15]. Several studies has been conducted to entrap carbonaceous material such as activated carbon (AC) [16], multiwall-carbon nanotubes (MWCN) [17-19], grapheme

oxide (GO) [20], ash [21], graphite nanocarbon (GNT) [22] and lignocellulosic biomass [23, 24] into biopolymer beads alginate [25]. However, AC, MWCN, GO, ash and GNT have complex synthesis process and, therefore, less economic viability on an industrial scale.

Among available lignocellulosic biomass, mangosteen, botanical name *Garcinia mangostana*, belongs to the family Clusiaceae and genus Garcinia. Mangosteen gives fruit which contains 25-30% edible part and the remaining 60-75% is a dark or light purple color peel [26] . Mangosteen trees are most abundantly grown in South East Asian countries such as Thailand, Malaysia and Indonesia [27] . It has a nice taste, can be eaten fresh, and can be used to produce wine, jam, preserves and puree. It has extensive medicinal value and used in treatment wound healing, diarrhea, fever, eczema and many other diseases. The Malaysian Ministry of Agricultural and Agro based industry has stated that 1 kilo of mangosteen fruit can produce about 0.6 Kg of MP waste[28], which is renewable, easily accessible, and relatively inexpensive. This MP waste can be used as adsorbent in various forms (powder, beads, and membranes) [16, 29, 30]. Problems associated with MP includes improper disposal and burning in open atmosphere, which can create environmental problems. Recent literature has shown that MP and MP based adsorbents efficiently remove methylene blue (MB) dye from aqueous media. With a higher adsorption efficiency, MP and MP-based adsorbents can be used as a low cost, efficient and easily available material for adsorption purpose. However, the MP powder is not suitable from an engineering point of view because of regeneration and recyclability issues. Therefore, its encouraged to use powder in the form of beads or membrane for dye extraction from water stream because of ease regeneration and recyclability.

To the best of our information, no previous literature that addresses MP powder in alginate for MB dye removal exist. The main goal of this research work was to synthesize mangosteen peel-alginate beads (MPAB) for efficient removal of MB dye from aqueous solution. MPAB were systematically characterized using BET surface area analysis, SEM, TGA and FT-IR. Process parameters, such initial pH of MB solution, MPAB dose, contact time, initial concentration of MB, and temperature, were studied and optimized. To find the feasibility and spontaneity of the adsorption process, theoretical studies of adsorption kinetics, adsorption isotherms, and thermodynamics were performed.

2. Experimental

2.1 Materials

AC prepared from MP waste was used. All chemicals used in this research work were used without any further processing. Methylene blue, HCl and NaOH were purchased from

R&M chemical, and $CaCl_2$ was purchased from Merck Germany. Sodium alginate (Mol. Wt. 120,000-190,000 g/mol, viscosity 15-25cP, 1% in H_2O) was purchased from Sigma-Aldrich.

2.2 Preparation of MPAB

The MP-alginate beads were synthesized from MP powder mixed with sodium alginate in a 2:1 ratio in distilled water. The MP powder and Na-alginate were mixed thoroughly in a petri dish and then slowly added to the distilled water in many steps. The slurry of MP and alginate was stirred at 400 rpm for 5 h, which resulted in a clear solution. The slurry was then sonicated for 30 min to remove the trapped bubbles present in slurry. The slurry was added dropwise to the 5% solution of $CaCl_2$ which resulted in the synthesis of spherical gel MPAB via cross linking. To ensure complete cross linking, the MPAB beads were stirred for 24h in cross linker solution. After 24h of this cross-linking process, the beads were removed from the $CaCl_2$ solution and washed with excess deionized water to ensure that no $CaCl_2$ molecules were left over on the MPAB surface. The synthesized MPAB was dried in an oven at 60^{o}C. The average size of MPAB was approximately 1.30 mm. The synthesized beads were placed in air sealed glass bottle and used for adsorption study of MB. **Figure 1** shows photograph of synthesized MPAB.

Fig. 1.

2.3 Characterization of the MPAB

The synthesied materials can be characterized by using different types of instruments before its targeted adsorbent application. These various material surface properties help to explain the adsorbtion data. Surface properties of MPAB were measured using a surface area and pore size analyzer (Micromeritics ASAP 2020) with 150 ^{o}C degassing temperature for 6 h. FTIR (Perkin, Elmer, Frontier) was used to identify surface active/functional groups available on the on the surface of MPAB before and after adsoption. FTIR spectra of the beads were measured in the region with range from 4000 to 400 $cm^{-}1$ in inert atmosphere by mixing the beads with KBr pellet. SEM (Zeiss Supra55 VP) was used to study surface morphology of synthesized MPAB. Thermal stabiliy of beads was measured using a Perkin Elmer, ASTA 6000 thermogravimetric analyzer (TGA) in inert atmosphere of nitrogen with a temerature range from 50 to 800 ^{o}C and a 10 ^{o}C/min heating rate.

2.4 Batch adsorption tests

To calculate the adsorption effeciency, the adsorption effeciency of beads were performed under different experimental conditions. A predetermined amount of beads were added to 20mL MB solution having specific concentration under room temperature. The flask

was placed in orbital shaker and was shaken at 150 rpm. At completion of each specific adsorption experiment, about 2 mL of MB solution was taken out from the flask with a syringe and put into a UV-Vis vial. The vial was placed in UV-Vis spectrophotmeter for measurement of MB concentration. The concentration of MB in bulk solution was determined by a UV-Vis spectrophotometer (Shimadzu 1800) at 664 nm using standard MB curve with the regression coefficient of the standard plot 0.998. The percentage removal (% R), adsorption capacity (q_t) and adsorption capacity at equlibrium were measured using the below equations [31]:

$$\%R = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \quad (1)$$

$$q_t = \left(\frac{C_i - C_f}{m}\right) \times V \quad (2)$$

$$q_e = \left(\frac{C_i - C_f}{m}\right) \times V \quad (3)$$

Where C_i and C_f ($mg.L^{-1}$) is the initial and final MB concentration, m (g) is the mass of adsorbent and V (L) is the volume of MB solution used in the adsorption experiments. To ensure maximum adsorption capacity of beads for MB adsorption, the effect of process parameters such as pH of initial MB solution (2-10), adsorbent dose (0.01-0.08g), contact time (60-1320 min), initial MB concentration (20-100 mg/L), and temperature (298.15-333.15K) were studied and optimized. The beads were recycled and reused by using a solution of NaCl (0.5M) and methanol mixed in the same volume ratio. The beads were recycled and reused five times. The desorption was calculated by the following formula:

$$\%\ Desorption = \frac{Mass\ of\ desorbed\ MB}{Mass\ of\ adsorb\ MB} \times 100 \quad (4)$$

2.5 Theoretical study

To better understand bead MB adsorption, kinetic, isotherm and thermodynamic studies were performed. For kinetic study of adsorption of MB on MPAB beads, a predetermined amount of beads was mixed with a specific amount of MB solution with a concentration in a range from 20 ppm to 100 ppm and was shaken for varying intervals of time, ranging from 60 min to 1320 min. The experimental data for MB adsorption on beads was procured by using two well-known pseudo-first order (PFO) [32] and pseudo-second order (PSO) [33] kinetic models. During the isotherm study, the adsorption experiments were run at different concentrations of MB solution in a range from 20 mg/L to 100 mg/L under optimized conditions until equilibrium was reached. The equilibrium data obtained in this study for the removal of MB on MPAB were analysed using four well kown adsorption isotherms models:

Langmuir [34], Freundlich [35] Tempkin [36] and Harkins-Juar [37]. To study the thermodynamics of adsorption of MB on MP-alginate beads, MPAB mixed with MB solution were run at various temperatures ranging from 298.15 to 333.15 K under optimized experimental conditions. Changes in various thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) for MB adsorption on MPAB were calculated in order to examine the spontaneity of a process.

3. Results and Discussion

3.1. Physical Characterization of MPAB

3.1.1. FTIR study

The active groups present on the MPAB surface were analyzed using FTIR analysis. **Figure 2.** shows the FTIR spectra of MPAB before and after MB adsorption. The peaks appeared at 3419 cm^{-1} (O-H group stretching), 2927 cm^{-1} (aliphatic C-H stretching vibration), 1613 cm^{-1} (C=O stretching vibration) and at 1036 cm^{-1} (-OH alcoholic) [38]. After MB adsorption, the stretching vibration of peaks -OH and -C=O groups due to intermolecular hydrogen-bonding with MB molecule are shifted from 3419 to 3412 cm^{-1} and from 1627 to 1613 cm^{-1}, respectively. Similar adsorption phenomena for MB on alginate beads have already been reported in literature [8, 39]. Owing to electrostatic attraction between MB and MPAB, the intensity of peaks located at 1613 cm^{-1} and 1036 cm^{-1} is considerbly decreased [8]. An oxygen containing functional group haas a peak at 1437cm^{-1}, corresponding to stretching vibration of $-COO^-$, considerable decrease in intensity after MB adsorption. This decrease in intensity is due to the extinction of some of $-COO^-$ groups involved in MB molecules adsorption [40, 41]. MB and others cationic dyes due to planner structure can be easily adsorbed on the adsobent surface by van der Waals forces. The FTIR analysis confirmed that MPAB contain a large number of hydroxyl and carbonyl groups, which are considered active interaction sites that interact with MB and others cationic dyes.

Fig. 2

3.1.2 Morphology of MPAB

FESEM technique was used to determine morphological properties and surface features of MPAB. **Figure 3** shows the FESEM micrographs of MPAB taken under different magnifications. The FESEM photographs show that the composite beads of MP-alginate have a rough surface that contains numerous bulges and cracks. Generally, the surface observed in this study are very common and observed by others researchers of alginate beads [38, 39].

To study the surface porosity such as surface area and pore sizes of MPAB**,** N_2 adsorption-desorption for MPAB were performed. N_2 adsorption-desorption isotherm for MPAB is shown in **Figure 4a**. The BET result indicated that beads follow type IV adsorption-desorption isotherm, showing mesoporous (2-50 nm) nature of synthesized beads [42]. The hysteresis loop also suggests that the MPAB beads are mesoporous in nature, with a pore diameter in the range of mesoporous according to IUPAC classification [43]. The BET surface area and Langmuir surface area for MP-alginate beads was 0.725 m^2/g and 1.26 m^2/g, respectively. An adsorbent's having a mesoporous structure is consider good to adsorb large molecules of various types of dyes, proteins, and polycyclic aromatic compounds [10].

3.1.3 TGA analysis

TGA was used to investigate the thermal decomposition behavior of MP powder and MP immobilized in alginate beads. Thermal properties of MP and MPAB measured in the temperature range of 50 - 850 ^oC are shown in **Figure 4b.** The small weight loss in both samples below 105 ^oC is due to vaporization of volatile organic compounds and moisture attached on the surface of MP and MPAB surface. The samples of both MP and MPAB are stable below 190 ^oC [44, 45].. The TGA curve shows one predominant weight loss and major degradation occurring in region from 190 ^oC to 360 ^oC [20, 21]. Thermal degradation of MPAB in this region might be due to the loss of water vapors trapped inside the beads [46]. The result demonstrated that the MPAB is thermally more stable than MP powder at all temperatures except in the temperature range from 190 to 320 ^oC. In the second stage, the maximum thermal degradation of both samples takes place. This major thermal degradation is due to degradation of cellulose and hemicellulose present in both samples [1]. It seems that alginate cause increase in thermally stability of MP. Vecino et al. [47] also observed same trend of TGA for vineyard pruning waste immobilized in alginate and found that these beads are thermally stable below 200 ^oC. Sargin et al. [48] also noticed an increase in thermal stability of microfungal spores composite beads.

Fig. 4

3.2. Adsorption Study

3.2.1. Adsorbent dose effect

MB adsorption as function of MPAB dose (0.01- 0.08 g) is represented in **Figure 5a**. The adsorption experiment was run for 60 min using pH 10. It was discovered that the adsorption capacity of beads for MB decreased from 137 to 22 mg/g while % R increase from 68.62 to 87.7% with the increase of MPAB. However, the decrease in adsorption capacity might be due to availability, or lack thereof, of free active sites after adsorption of all dye's

molecules and an inverse relation between adsorption capacity and adsorption dose, as shown in Eqn. 2. The increase in %R of MB with increase of adsorption dose is due to migration of many molecules from liquid phase to solid phase The findings are very common and similar findings are reported elsewhere in literature [49].

3.2.2 pH effect

Initial pH of MB solution plays a very key role in adsorption, and therefore it is a priority to understand the effect of pH on MPAB adsorption. The pH of MB solution was varied from 2 to10). Effect of initial pH of MB solution on beads performance is shown in **Figure 5b**. Results, provided in Figure 6, clearly indicate that adsorption efficiency of beads for MB is greatly affected by pH. The adsorption of dye on the surface of adsorbents occurs due to electrostatic attraction that exists between MB cation and a negatively charged presence on adsorbent surface. Initial pH of MB solution has considerable effect on MB removal. The adsorption capacity of MB on MPAB jumps from 141.5 to 182 mg/g when pH of solution increases from 2 to 10. In acidic pH region (below pH 6), the low adsorption efficiency of MPAB for MB dye adsorption is due to the competition of H^+ ions and MB molecules to bind with active sites. However, with an increase of pH from acidic to basic region (above pH 7), the adsorption capacity considerably increases. The highest adsorption capacity was noted at pH 9.5. This increase in adsorption efficiency is due to the increase in negatively charge on the surface of MPAB. This increase in negative charge on the adsorbent surface can increase the interaction of MB cations with the surface of MPAB. However, the uptake of MB slightly increases with the increase of pH of solution greater than 8. Therefore, initial pH of MB solution was selected as 9.5. The removal capacity of MB dye on various types of adsorbents in a basic pH range has already been reported in literature elsewhere [50]. Maximum adsorption of MB for alginate/activated carbon was observed at pH 10 [38].

3.2.3 Initial concentrations and contact time effect

To optimize adsorption conditions for dye removal from aqueous phase to solid phase, the study of contact time and solution concentration is considered crucial. The effect of initial MB concentration (20 - 100 mg/g) and contact time (60-1320 min) on adsorption efficiency of MPAB (pH 9.5, adsorbent dose 0.01 g and 25 ^{o}C) is shown in **Figure 5c**. The results confirmed the quick adsorption of MB dye occurred early in time. High adsorption efficiency at initial contact time is fast due to high mass transfer and rapid approach of MB cations to the surface of MPAB and coverage of more active sites with cations of dye at early stage. However, as contact time increases, elimination of MB from aqueous solution decreases due to the

saturation of active sites of adsorbent with dye molecules. The adsorption capacity of MB on MPAB is fast until 600 min and very small increase was observed after 1080 min. Zhuang et al. [50] found a decrease in removal of MB dye on GO/alginate beads with higher contact time between MB and beads, and equilibrium was achieved after 1200 min. The results in Figure 7 shows that the removal efficiency of beads for MB increases from 83 mg/g to 185 mg/g with the increase of dye concentration from 20mg/g to100 mg/g. This increase is due to the presence of more MB cations in the solution that interact and bind with the active surface functional groups of adsorbent surfaces. This increase in adsorption capacity of beads for MB is very normal and is extensively reported by other researchers elsewhere [16, 51].

Fig. 5

3.3 Kinetic Study for MB adsorption

To study the kinetics of MB adsorption on MPAB, PFO (Eqn. 4) and PSO kinetic models (Eqn. 5) were applied for the experimental data of MB on beads [32].

$$log(q_e - q_t) = log q_e - \frac{k_1}{2.303} \times t \quad (4)$$

where k_1 is the pseudo first order rate constant and q_e and q_t ($mg.g^{-1}$) are the amounts of MB adsorbed at equilibrium and at time t (min), respectively. The plot of $\log(q_e - q_t)$ gives the values of q_e and k_1.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Whrere q_t (mg/g) is the amount of adsorbed MB on MPAB at time t (min). The rate constant k_2 for pseudo second order model and q_e can be deduced from the intercept and slope of the plot t/q_t and t. **Figure 6** shows the linear plots obtained for MB adsorption at various times using PFO and PSO kinetic models while Table 1 shows the various kinetic parameters obtained for MB adsorption. The value of R^2 (0.997) shows that MB adsorption on MPAB is well fit by pseudo second order kinetic model. In addition, the theoretical value of adsorption capacity calculated for various concentration of MB removal on MPAB is close to the experimental values. This close agreement between the experimental and theoretical values of adsorption capacity supports that MB adsorption on MPAB is well fit by the PSO kinetic model (**Figure 6b**). Khanday et. al. also observed that PSO kinetic model well described the MB adsorption on activated palm oil ash/zeolite/chitosan beads [13].

Fig. 6

Table 1.

3.4 Adsorption isotherm study

The equilibrium data obtained in this study for MB adsorption on MPAB were analysed using Langmuir [34], Freundlich [35] Tempkin [36] and Harkins-Juar [37] isotherms. Linear form of Langmuir isotherm model is shown in Eqn. 6 as given below:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}} \times C_e \quad (6)$$

where C_e (mg/L) is MB concentration, q_{max} (mg/g) is maximum amount of dye adsorbed, and b is referred as Langmuir constant. The slope and intercept of the plot of C_e/q_e and C_e gives the values of q_{max} and b, respectively. The empirical relationship of q_e and C_e is determined from the Freundlich isotherm model, which explains the heterogeneity of the system. Eqn. 7 can explain the Freundlich isotherm model:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (7)$$

Where K_F and 1/n are the Freundlich isotherms constants and represent adsorption capacity and intensity, respectively. The linear plot drawn for various adsorption isotherms is shown in Figure 9. Various thermodynamic parameters obtained from the linear plot of Freundlich and Langmuir adsorption isotherms are given in Table 2. The slope and the intercept of linear plot of lnq_e versus lnC_e give the values of both of n and K_F. The values of n and K_F are displayed in Table 2. The value of n for MB adsorption on beads is greater than 1, which confirm the convenient adsorption and heterogenity of adsorption. The regression coefficients obtained for adsorption of MB using beads are relatively close to each other and greater than Tempkin and Harkin-Jura adsorption isotherms. The removal of MB on MPAB is fitted by both of the applied isotherm models, confirmed from the value of the correlation coefficient obtained (R^2) for Langmuir (0.995) and Freundlich (0.989) isotherm models.

Fig. 7

Table 2.

3.5 Thermodynamic study

3.5.1 Temperature effect

Temperature significantly affects the adsorption capacity of MPAB for MB dye. To find the effect of temperature on the removal efficiency of beads for MB, the adsorption experiments were performed under different temperatures ranging from 298.15 K to 333.45 K, using optimized experimental conditions. The temperature effect on MB adsorption on MPAB is displayed in **Figure 8a**. The capacity of adsorption of beads for MB removal at 298, 303,

313, 323 and 333 K were 185, 1801, 177, 166 and 151 mg/g, respectively. The result demonstrated that an increase in temperature causes a decrease in the MB uptake from aqueous solution. With an increase of temperature, dye molecules have a higher energy which might cause a decrease in attraction with adsorbent surface. The decrease in adsorption capacity of MB onto MPAB at higher temperature indicates the exothermic nature of the adsorption. Thermodynamic parameters calculated for MB removal by MPAB can be determined by performing adsorption experiments under various temperatures. Eqn. 12 was used for calculation of Gibbs free energy. Other thermodynamic parameters, such as entropy and enthalpy for adsorption process, can be calculated by plotting $\ln K_c$ versus 1/T using Eqn. 13. (**Figure 8b**).

$$K_c = \frac{q_e}{C_e} \tag{11}$$

$$\Delta G^0 = -RT ln K_c \tag{12}$$

$$ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{13}$$

Where T is the absolute temperature in K, K_c is the equilibrium constant and R is the general gas constant (8.314 $J.mol^{-1}.K^{-1}$). The calculated values of Gibbs free energy were -7.93, -7.36, -7.14, -6.08 and -5.06 KJ/mol at 298, 303, 313, 323 and 333 K, respectively (**Table 3**). The negative value of ΔG° revealed the spontaneity of adsorption process. The chemical or physical nature of adsorption of MB can be determined by the value of ΔG°. The value of ΔG° in the range of -20 KJ/mol to 0 KJ/mol, indicated the physical nature of MB adsorption on beads. The -ve values of ΔS^o and ΔH^o gives information that the adsorption of MB on MPAB is spontaneous and exothermic [52]. The negative ΔS° value indicate the decrease in randomness at MPAB interface as a result of MB adsorption [24, 38].

Fig. 8

Table 3.

3.6 Recyclability and reusability of beads

The worth of an adsorbent in industrial use is increased if said adsorbent is recyclable and reusable. The adsorbents were recycled and reused five times without any considerable decrease in adsorption efficiency. The first five adsorption capacities for beads were 95%, 92%, 90%, 85% and 80%, respectively. This finding confirmed that our synthesized beads are easily recyclable and reusable, which decreases the capital cost of the process.

3.7 Comparison with other beads

Several adsorbents have been reported in the literature for MB adsorption from aqueous solution. **Table 4.** shows comparison of the MPAB with alginate beads already reported in literature [15, 20, 53-60]. The results given in Table 4 confirmed that MPAB shows competitive adsorption ability and affinity for MB in comparison to already reported adsorbents in literature. Moreover, the synthesized MPAB is a novel, competitive, and cost-effective adsorbent for MB adsorption. Therefore, it is recommended to use MPAB for removal of MB and other cationic dyes similar to MB.

Table 4.

4. Conclusion

In the present research work, MP waste was successfully encapsulated in alginate beads and used as an effective adsorbent for MB adsorption. The SEM and BET analysis confirmed that the beads are mesoporous in nature and have a porous surface. The FITR analysis confirmed that synthesized beads have nucleophilic sites on the surface which are capable of attracting MB molecules from aqueous phase. The adsorption study confirmed that MPAB composite has the potential to efficiently adsorb MB from aqueous solution. It has been concluded from the experimental results that MB adsorption significantly depends on initial pH of MB solution, contact time, initial MB concentration, and temperature. The adsorption capacity was found to increase with an increase in pH from acidic to basic conditions, contact time, and initial concentration of MB solution. Kinetic study confirmed that a PSO model well explained the adsorption of MB on the beads. Moreover, both Freundlich and Langmuir isotherms models described well the isotherm data of adsorption. Conclusively, we can claim that MPAB composite can be effectively applied as a low cost, potential, sustainable and environmentaly friendly sorbent for the effective removal of MB and other cationic dyes.

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Table 1. Pseudo first and pseudo second order model parameters for adsorption of MB on MPAB

	Pseudo-first order kinetic				Pseudo-first order kinetic		
C_o	q_{exp} ($mg.g^{-1}$)	qcal ($mg.g^{-1}$)	k_1 (min^{-1})	R^2	q_{cal} ($mg.g^{-1}$)	k_2 ($g.min.mg^{-1}$)	R^2
20	38.28	41.30	0.0069	0.960	39.88	0.000598	0.997
40	75.98	172.99	0.0110	0.937	80.97	0.000197	0.995
60	113.49	175.81	0.0072	0.925	124.68	7.88E-05	0.992
80	149.55	213.80	0.0068	0.896	161.81	7.18E-05	0.995
100	184.938	152.63	0.0045	0.960	197.62	5.80E-05	0.995

Table 2. Langmuir, Freundlich, Harkins Jura and Tempkin isotherms model parameters for adsorption of MB on MPAB.

Type	Linear form	Plot	parameters
Langmuir	$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$	$\frac{C_e}{q_e}$ vs C_e	Q_o (mg/g) = 373.00 b (L/mg) = 0.131. R^2 = 0.995
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	$\ln q_e$ vs C_e	n = 1.35 K_F (mg/g) = 44.69 R^2 = 0.989
Tempkin	$q_e = B\ln A + B \ln C_e$	q_e vs $\ln C_e$	B= 68.648 A = 1.712 R^2 = 0.934
Harkins Jura	$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e$	$\frac{1}{q_e^2}$ vs $\log C_e$	B= -0.759 A= -1466.05 R^2 = 0.764

Table 3. Thermodynamic parameters for adsorption of MB on MPAB.

T (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^0 (J/mol.K)
298	-7.93		
303	-7.36		
313	-7.15	-31.48	-77.47
323	-6.08		
333	-5.06		

Table. 4 Comparison of adsorption capacity of MPAB with reported alginate beads

Adsorbents	q (mg/g)	Reference
GO/Ca-alginate composites	181.81	[19]
Kappa-carrageenan/poly(glycidylmethacrylate) hydrogel beads	166.62	[54]
Alginate-halloysite nanotube beads	250	[55]
Apatite/Attapulgite/Alginate Composite Hydrogel	244.6	[56]
Sericin-derived activated carbon (S-AC)/Alg beads	502.5	[57]
Palmarosa entrapped in alginate beads	6.45	[50]
Cellulose nanocrystal–alginate hydrogel beads	256.41	[51]
Alginate-derived carbon beads	397.9	[52]
Alginate-coated perlite beads	104.	[53]
Pleurotus mutilus Immobilized as Calcium Alginate Biobeads	23	[15]
Mp-alginate beads	373	Present study

LIST OF FIGURES

Fig. 1. Typical photograph of MPAB.

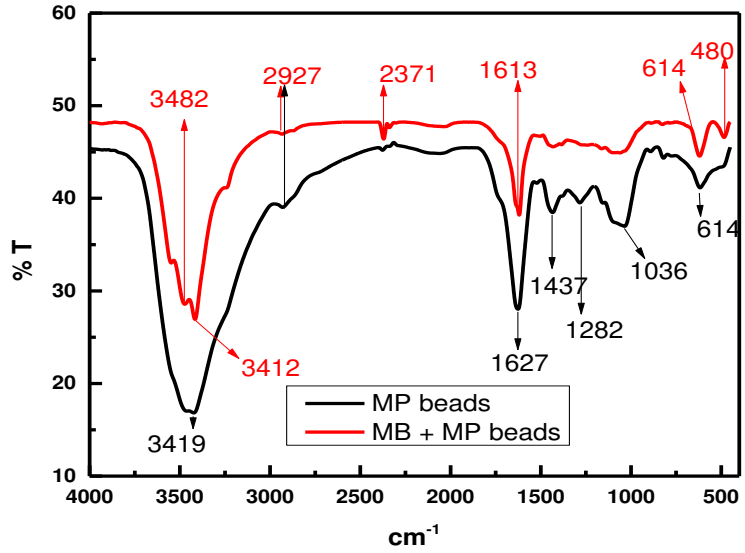

Fig. 2. FTIR spectra of MPAB before and after MB adsorption.

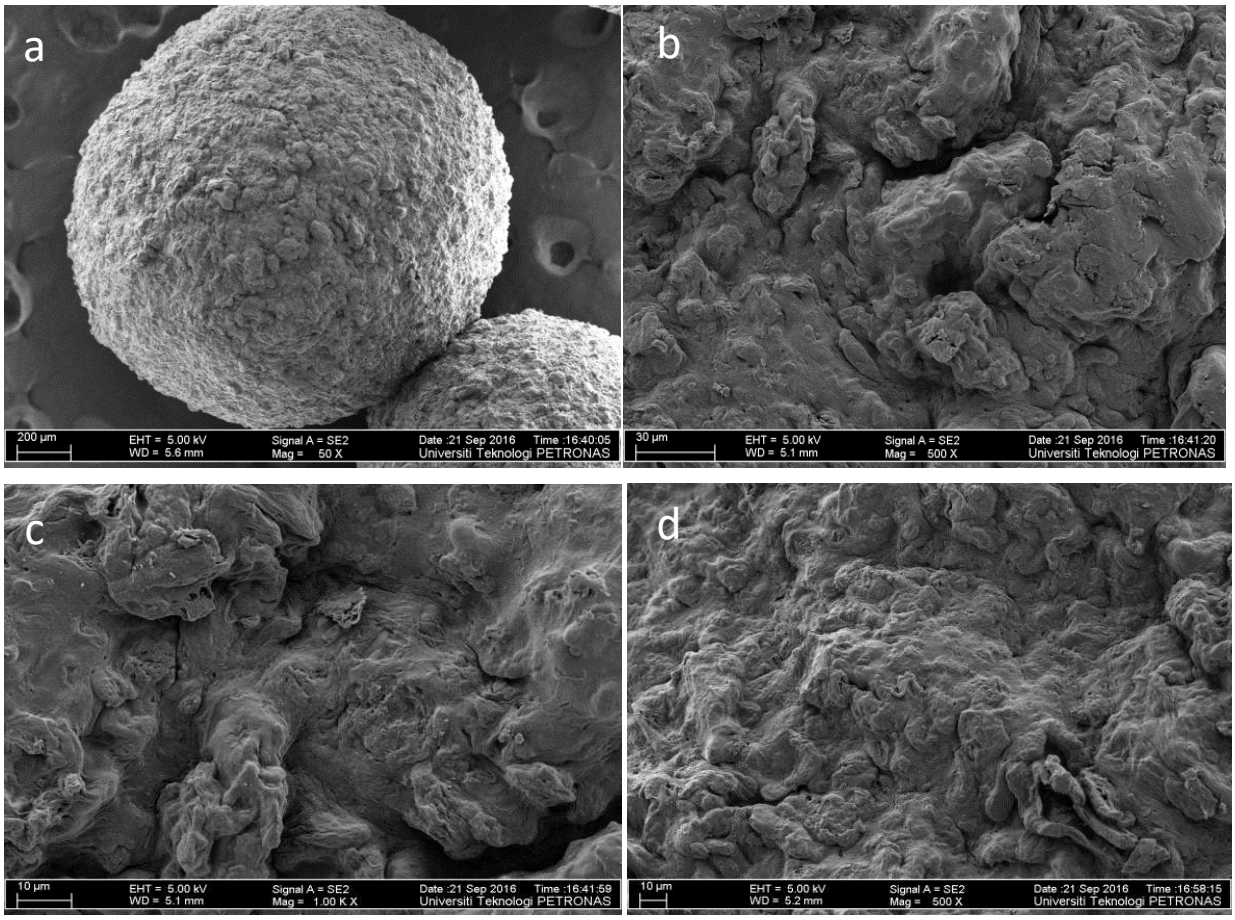

Fig. 3. SEM photographs analysis of MPAB.

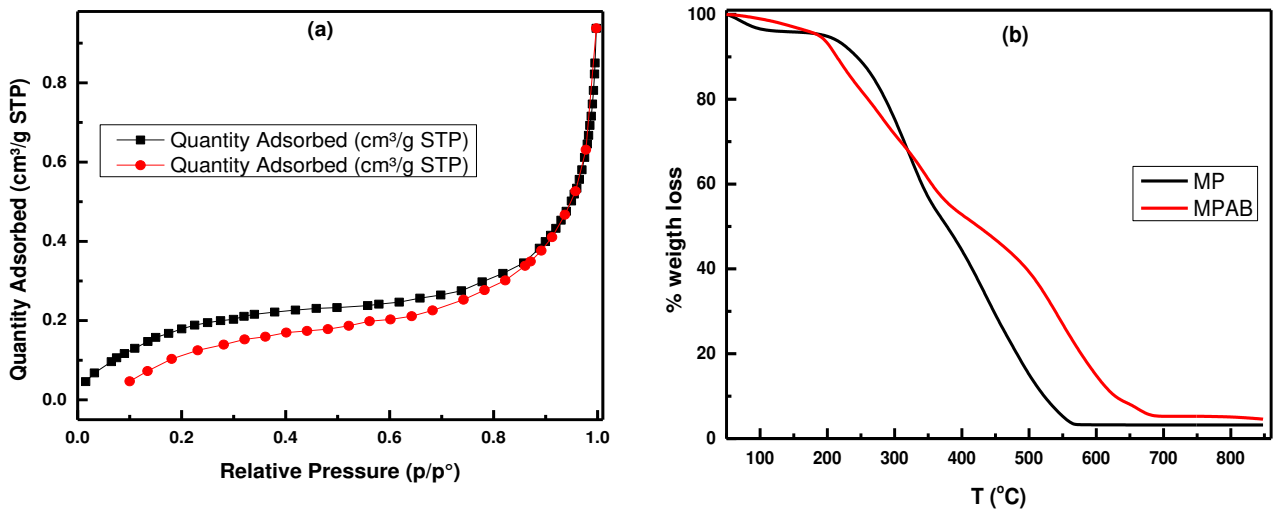

Fig. 4. (a) N_2 adsorption–desorption isotherms and (b) Thermal degradation of MPAB

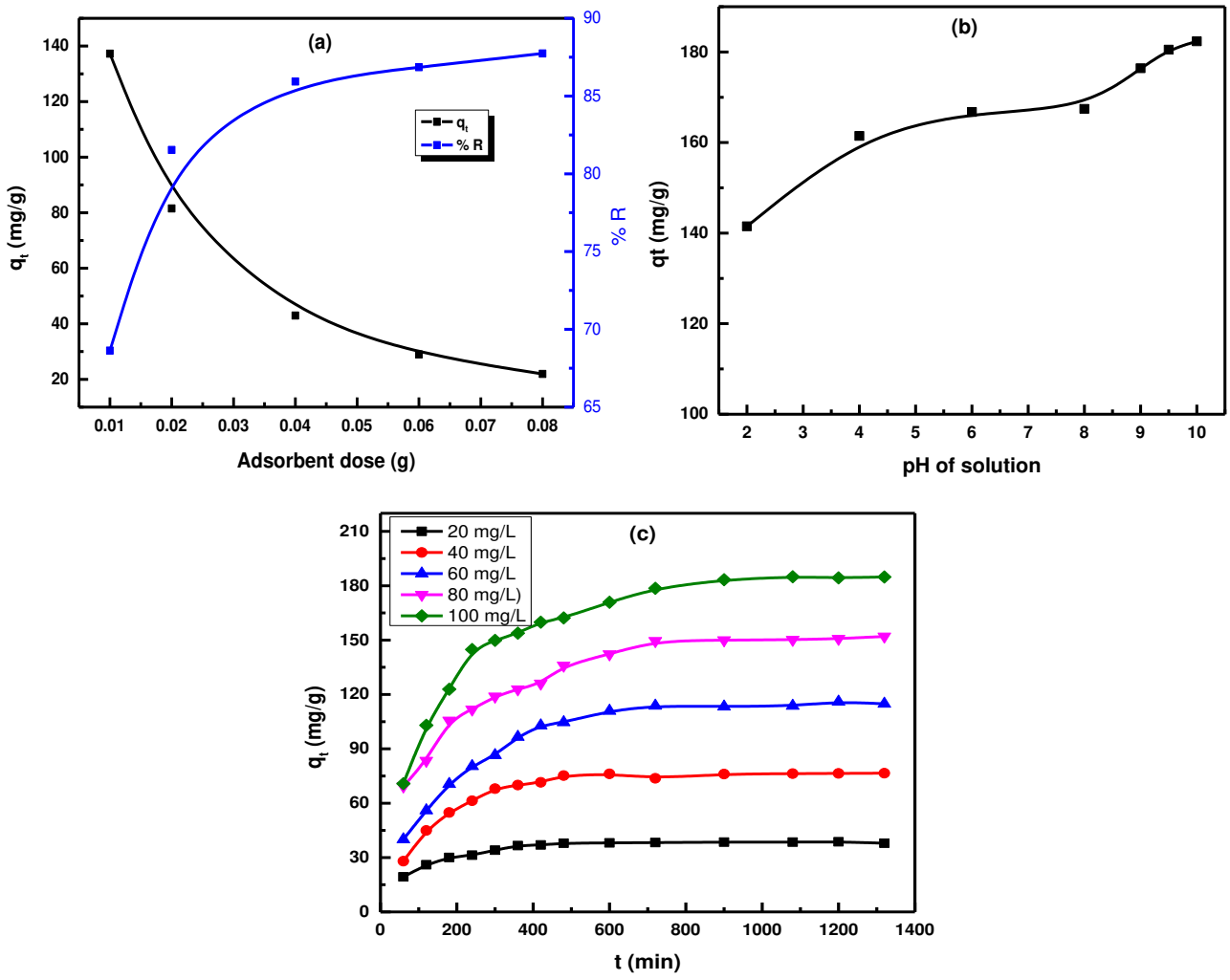

Fig. 5. Effect of (a) adsorbent dose and (b) initial pH and contact time on MB adsorption on MPAB.

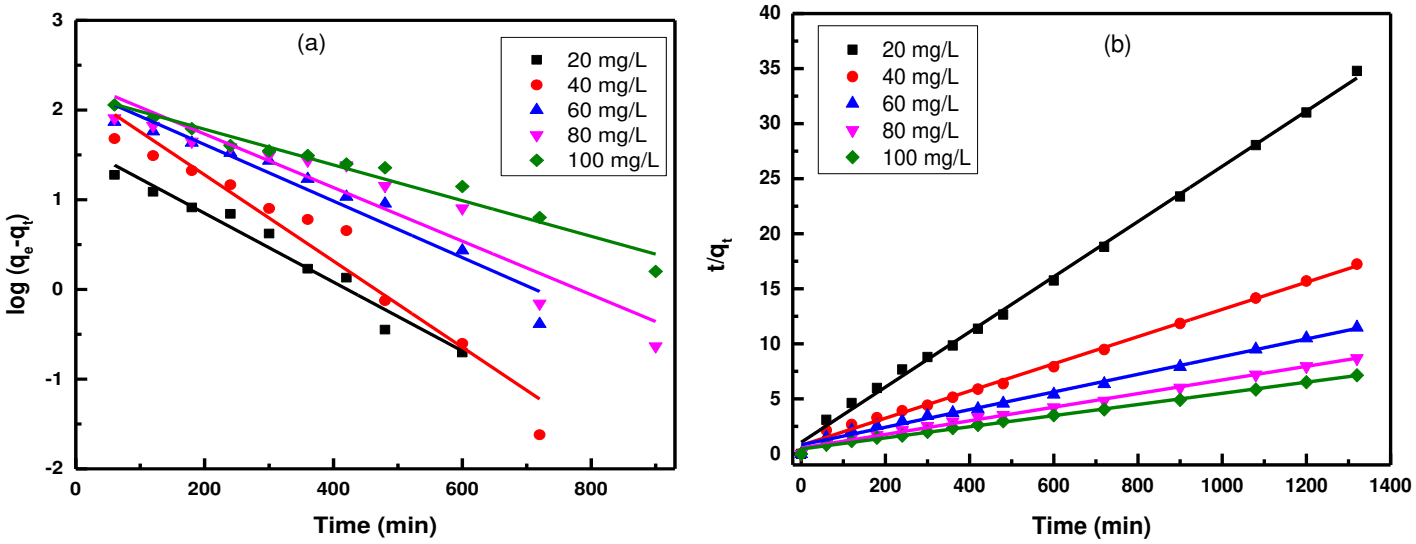

Fig. 6. (a) Pseudo first and (b) pseudo second order kinetic plots for adsorption of MB on MPAB.

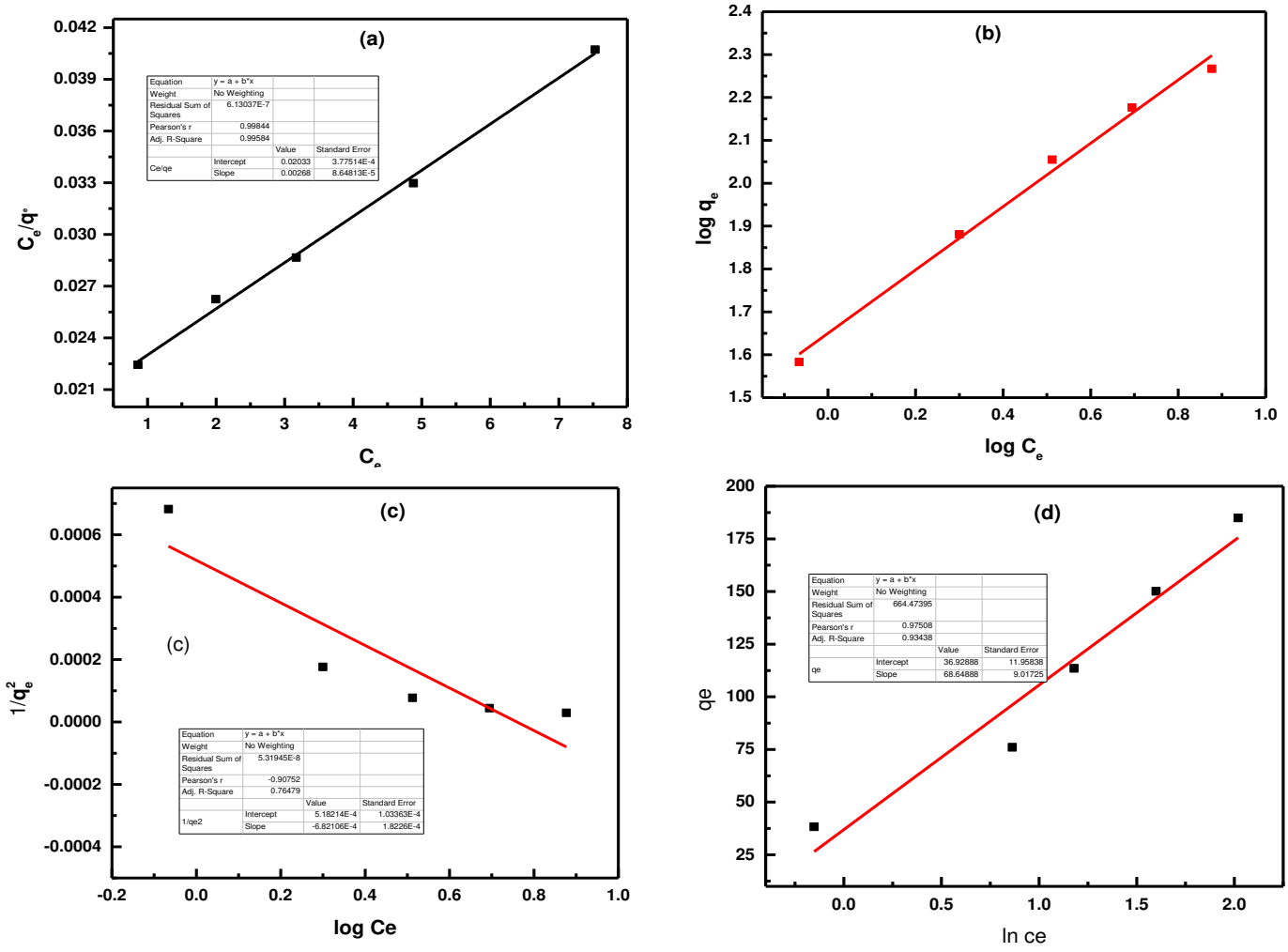

Fig. 7. (a) Langmuir, (b) Freundlich, (c) Harkins-Jura and (d) Tempkin isotherms model for MB adsorption on MPAB.

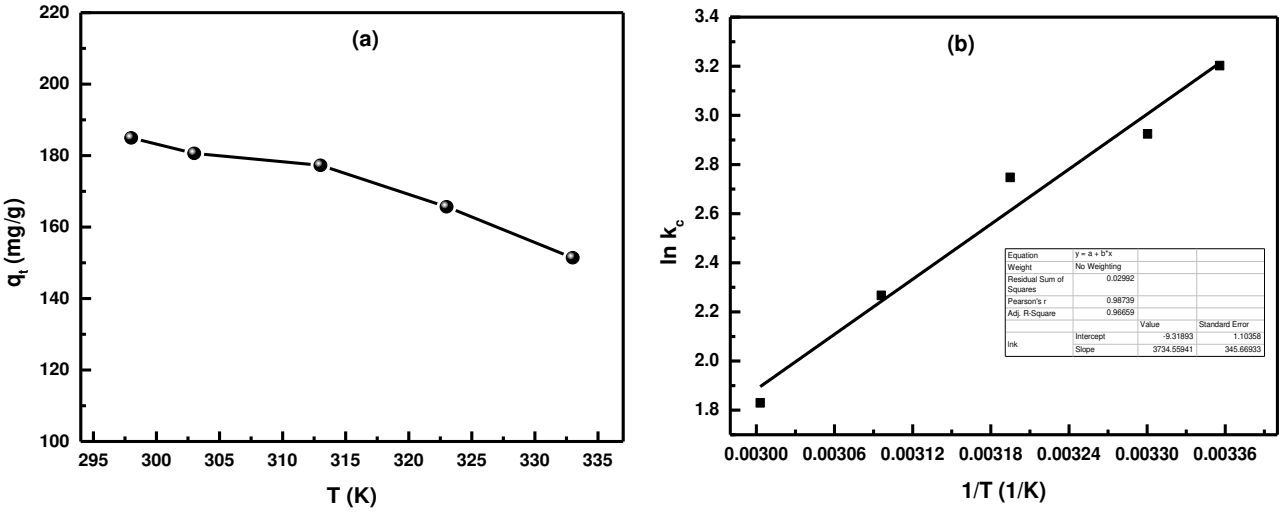

Fig. 8. Effect of temperature on MB adsorption and (b) Arrhenius plot for MB adsorption on MPAB

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