Materials Research Express

PAPER • **OPEN ACCESS**

Facile preparation of porous activated carbon under ultrasonic assistance for the Methylene blue removal from aqueous environment: characterization, isothermal, kinetic and thermodynamic studies

To cite this article: Hadi Eslami *et al* 2020 *Mater. Res. Express* **7** 015620

Materials Research Express

PAPER

Facile preparation of porous activated carbon under ultrasonic assistance for the Methylene blue removal from aqueous environment: characterization, isothermal, kinetic and thermodynamic studies

Hadi Eslami[1], **Rasoul Khosravi**[2,6], **Mohammad Reza Miri**[3], **Abdollah Gholami**[4], **Esmail Ghahramani**[5] and **Afshin Khosravi**[2]

[1] Occupational Environment Research Center, Department of Environmental Health Engineering, School of Health, Rafsanjan University of Medical Sceiences, Rafsanjan, Iran
[2] Social Determinants of Health Research Center, Department of Environmental Health Engineering, School of Health, Birjand University of Medical Sciences, Birjand, Iran
[3] Social Determinants of Health Research Center, Department of Health, School of Health, Birjand University of Medical Sciences, Birjand, Iran
[4] Social Determinants of Health Research Center, Department of Occupational Health Engineering, School of Health, Birjand University of Medical Sciences, Birjand, Iran
[5] Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
[6] Author to whom any correspondence should be addressed.

E-mail: hadieslami1986@yahoo.com **and** Khosravi.r89@gmail.com

Keywords: adsorption, activated carbon, dye, ultrasonic

OPEN ACCESS

RECEIVED
5 October 2019

REVISED
4 January 2020

ACCEPTED FOR PUBLICATION
9 January 2020

PUBLISHED
27 January 2020

Abstract

Powdered *Peganum Harmala* activated carbon (PPAC) was synthesized by a new activation method using ultrasonic waves (with a frequency of 37 KHz for 1 h) after carbonization and application to remove methylene blue (MB) from aqueous solutions. In this experiment, the characteristics of the PPAC were examined through BET, FESEM, and FTIR spectrum. The effects of the initial pH (2–12), the adsorbent's dose (0.5–4 g L^{-1}), reaction time (2–80 min), initial concentration of the dye (50–300 mg l^{-1}), mixing rate (0–300 rpm), and the solution's temperature (10 °C–50 °C) in adsorption process were investigated. The results indicated that ultrasonic waves have the significant effect on the carbon activating process. BET analysis indicated that the specific surface area of PPAC before activation was 0.776 m^2 g^{-1} and had increased to 442.14 m^2 g^{-1} following activation by ultrasonic waves. FESEM images showed that significant elevation of the porosity level and development of numerous pores in the activated carbon. FTIR analysis indicates that following the activation, –OH groups have been developed onto the PPAC surfaces. The adsorption isotherms and kinetics were well fitted by the Freundlich and pseudo-second order model. Investigation of thermodynamic parameters indicated that adsorption process of MB by PPAC is spontaneous, endothermic, and physical.

Nomenclature

C_0	initial MB concentrations (mg l^{-1})
C_e	final concentration of methylene blue (mg l^{-1})
C_t	MB concentrations at time *t* of reaction (mg l^{-1})
k_1	pseudo-first order rate constant (1 min^{-1})
k_2	pseudo-second order rate constant (mg (g $min)^{-1}$)
K_f	Freundlich adsorbent capacity (mg g^{-1} (l $mg^{-1})^{1/n}$)
K_L	Langmuir constant (l mg^{-1})

n	the reciprocal of reaction order
q_t	adsorption capacity at time t (mg g^{-1})
q_e	adsorption capacity at equilibrium conditions (mg_{MB} g^{-1}_{PPAC})
q_{max}	maximum adsorption capacity (mg g^{-1})
R	gas constant (8.314 J mol^{-1} K)
V	volume (L)
T	absolute temperature (K)
$\Delta G°$	Gibbs free energy change(kJ mol^{-1})
$\Delta H°$	enthalpy changes(J $mol^{-1}.k^{-1}$)
$\Delta S°$	entropy changes(kJ mol^{-1})
ρ	density of the solution (1000 g l^{-1})
K_d	thermodynamic equilibrium constant

1. Introduction

Methylene blue (MB) is a cationic dye and one of the most common dye contaminants widely used in various industries such as textile, paper, leather, cosmetics, plastic, printing, and food industries [1–3]. During dyeing process particularly in textile industry, large quantity of water is usually used thereby resulting to the production of large volume of dye wastewater. The removal of dye from wastewaters and aquatic environment is vital in the maintenance of human health and the environment due to their toxic, mutagenic and carcinogenic properties along with their adverse effect on photosynthetic process of water plant [4–6].

The common methods for removing dye compounds like MB from wastewaters include biological processes such as activated sludge, chemical processes such as coagulation and flocculation, electrocoagulation [7, 8], advanced oxidation processes such as ozonation, and membrane processes [9, 10]. Since dye molecules are non-biodegradable, application of biological processes for removing dye compounds is of no practical use [11]. On the other hand, chemical and advanced treatment methods are very expensive and thus are not cost-effective [12]. In recent decades, adsorption processes have been found appealing in a large number of applications since it is an effective and economical method requiring low levels of energy and requiring simple design and operation for removing dye contaminants from wastewater [13, 14]. Activated carbon is one of the most common adsorbents used for adsorption process due to its characteristic high specific surface and large adsorption capacity [15–17]. Nevertheless, the production and recovery of commercial activated carbon incurs large costs especially for developing countries. As such in recent studies, researchers have primarily been searching for inexpensive activated carbons obtained from agricultural byproducts and agricultural wastes [18–21]. The reason for utilizing agricultural byproducts as raw materials for producing activated carbon is that these compounds are renewable and have a lower cost for development [22]. *Peganum Harmala* is a wild plant abundantly found around Birjand City and can be utilized easily. Therefore, considering the abundance and structural characteristics of *Peganum Harmala* seed stated in the study by Khosravi *et al* [23], it can be a suitable alternative for producing activated carbon. Various methods like chemical method are required in order to trigger activated carbon. Although, in this study, ultrasonic waves have been employed as a different method of activation owing to its property of initiating intense thermodynamic condition at molecular state and creating changes in the structure of the adsorbent [24]. The effectiveness of the ultrasonic waves was determined by evaluating morphological properties and its specific surface. Similarly, to examine the characteristics of adsorption process, kinetics, isotherms, and thermodynamics of the process have also been explored.

2. Experimental

2.1. Paganum harmala powdered activated carbon preparation (PPAC)

The procedure of preparing the precursor (powdered *Peganum Harmala* Seed has been fully described in our previous study [23]. To produce activated carbon, a new physiochemical method employing ultrasonic technology was used for activation. In this technique, instead of using traditional, expensive and dangerous activation methods, a simpler and more economical method has been utilized. First, the powdered *Peganum Harmala* seed was fully impregnated with phosphoric acid 50% v/v solution and then soaked to ambient temperature for 48h [25]. Next, the impregnated powder was transferred to a cylindrical steel reactor with a lid so as to prevent the permeation of oxygen. The steel reactor was then transferred to a programmable furnace

(HL40P controller) and the furnace temperature was brought to 500 °C at a rate of 5 °C per minute, and maintained at this temperature for 2 h. After the furnace was cooled down, the reactor was taken out and the resulting powdered *Peganum Harmala* carbon (PPC) was immersed in HCL (3N) inside a 500-ml beaker for activation and transferred to an ultrasonic bath (Elmasonic E 30H) with a frequency of 37 KHz and then exposed to ultrasonic waves for 1 h. Thereafter, the resulting activated carbon was washed twice with distilled water in order to get to a pH of 6. The activated carbon (PPAC) was then exposed to a temperature of 110 °C for 2 h to be completely dried. The obtained activated carbon was finally kept in a desiccator for further usage.

2.2. Characterization of PPAC

In order to investigate the properties of the produced activated carbon and determine the effectiveness of this novel activation method, the following analyses were carried out on PPAC and PPC. To determine the morphology of the adsorbent's surface, Field Emission Scanning Electron Microscopy (FESEM) test was utilized using Mira 3-XMU. To determine and identify the functional groups present on the adsorbent, Fourier transform infrared spectroscopy test was employed using Spectrum RXI device (PerkinElmer, USA). The adsorbent's specific surface (Brunauer–Emmet–Teller; BET analysis) was performed by nitrogen adsorption-desorption isotherm at −250 °C using Belsorp mini II device (Bel Co., Japan).

2.3. The adsorption experiment

This research has been experimental and was conducted in a batch system in flask with a volume of 100cc on a shaker. Different concentrations of MB were prepared using 1000 mg l^{-1} of stock solution. In performing the experiment, 50 c.c. of the sample with a specific concentration was first extracted using graduated cylinder and then poured into a flask. When adjustment of pH was required, the pH of the solution was adjusted using 1N HCl and NaOH. Thereafter, a specific dose of the adsorbent was weighed and added into the flask which was then immediately placed on a shaker and the stirring rate regulated. Following the intended contact time, the sample was removed from the shaker and filtered through Whatman filter paper 0.45 micron. The filtered sample was employed for the measurement of the amount of the remaining dye. The most important variables investigated in this experiment have been the initial pH of the solution (2–12), the adsorbent's dose (0.5–4 g L^{-1}), reaction time (2–80 min), initial concentration of the dye (50–300 mg l^{-1}), mixing rate (0–300 rpm), and the solution's temperature (10 °C–50 °C). In order to guarantee replicability of the results, each stage of the experiment was replicated twice and the average of the results was recorded.

2.4. Method of analysis

In this experiment, the measurement of dye was done with colorimetric method using a spectrophotometer T80 + UV/VIS spectrometer at the wavelength of 665 nm based on the methods presented in the water and wastewater standard methods [26]. All of the materials used in this study were purchased from Merck Co. and data analysis was performed by Excel.

3. Results and discussion

3.1. Characterization of the adsorbent

N_2 adsorption—desorption isotherm and BJH pore size distribution of PAC and PPAC are shown in figure 1. According to the BET test, the specific surface area of PPC was equal to 0.776 m^2 g^{-1} and had increased to 442.14 m^2 g^{-1} following activation by ultrasonic waves (PPAC specific surface). Also, the mean pore diameter for PPC and PPAC were 15.82 and 2.11 nm, respectively. The high significant increase in the specific surface and decrease in pore diameter were observed as a result of performing activation process by the ultrasonic technique in the acidic environment indicating that this process could be experimented as a new method for improving specific surface in adsorbents. With this significant decrease in pore diameter and subsequently increase in the specific surface, a large number of new pores and sites are created in the adsorbent's surface [27, 28]**.** According to the molecular size of MB (0.84 nm) [29] and pore size of PPAC (2.11 nm) and also, a large number of new pores, therefore, the prepared PPAC adsorbent has the pores and surface area required to adsorb the MB molecules.

FESEM images for PPC (figure 2(a)) and PPAC (figure 2(b)) indicate that the activation process of PPC and its conversion to PPAC results in significant elevation of the level of porosity and development of numerous pores in the activated carbon. These created large pores are very effective in adsorption of dyes since they can accommodate the large molecules of dye inside them [30]. Moreover, these large pores developed a PPAC shown in figure 1(b) which allows for greater diffusion of solution across all sections of the adsorbent's surface, thereby increasing the adsorption capacity. In summary, it can be stated that this new activation method has led to great improvements in the adsorbent's properties. Hotspot theory was used to account for the reason behind the development of large pores [31]. According to this theory, in a liquid environment, ultrasonic waves can cause

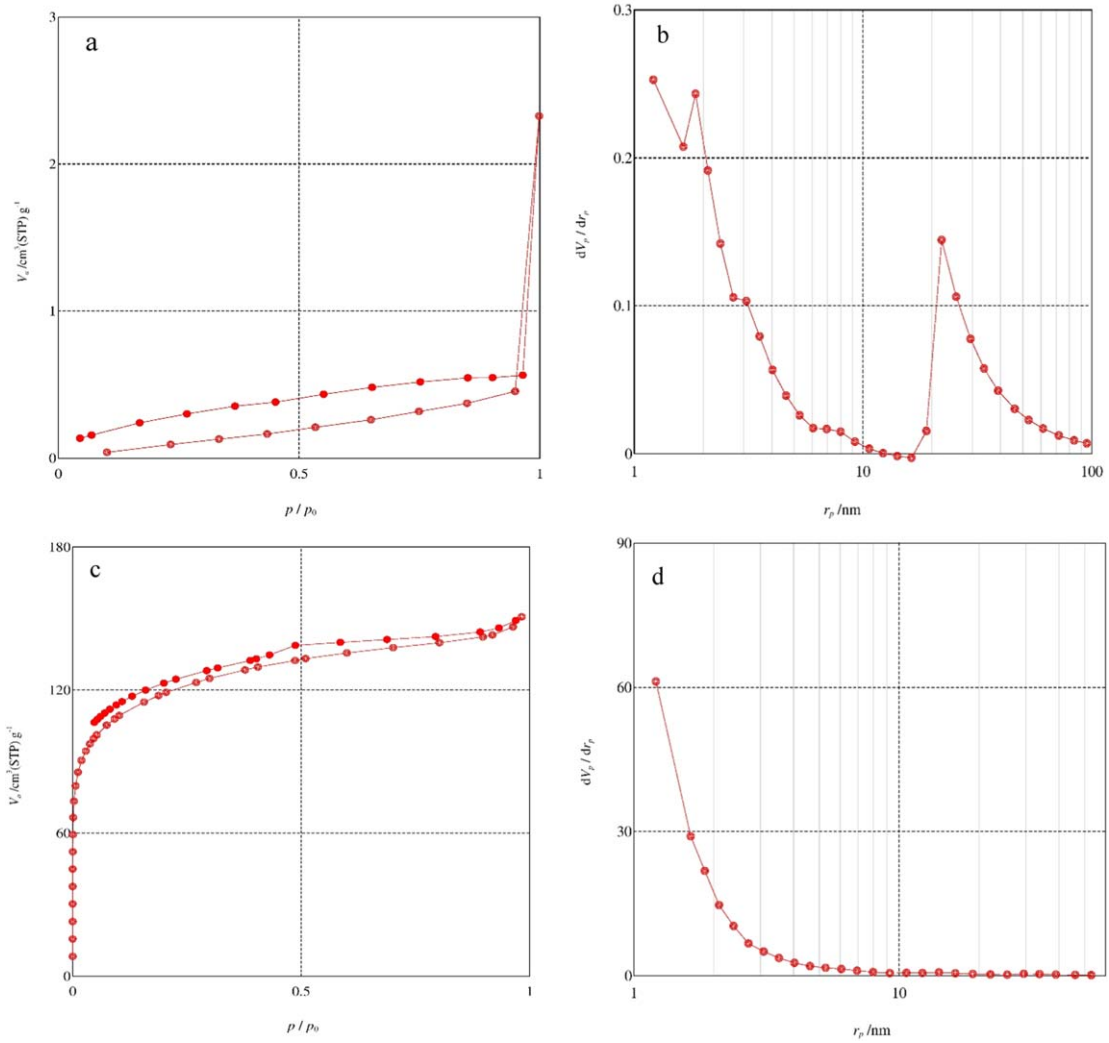

Figure 1. N_2 adsorption—desorption isotherm and BJH pore size distribution of PAC (a), (b) and PPAC (c), (d).

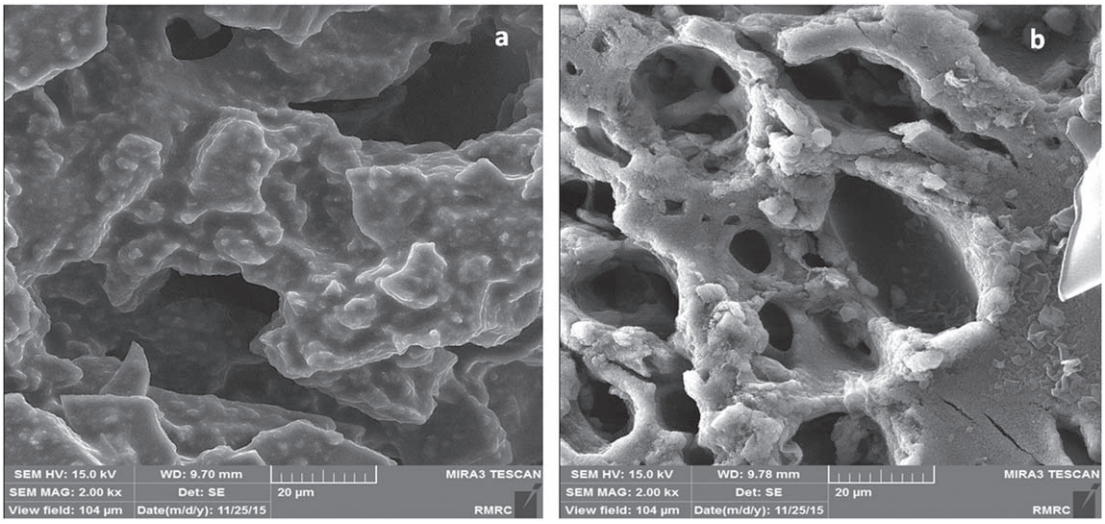

Figure 2. FESEM micrographs of PAC (a) and PPAC (b).

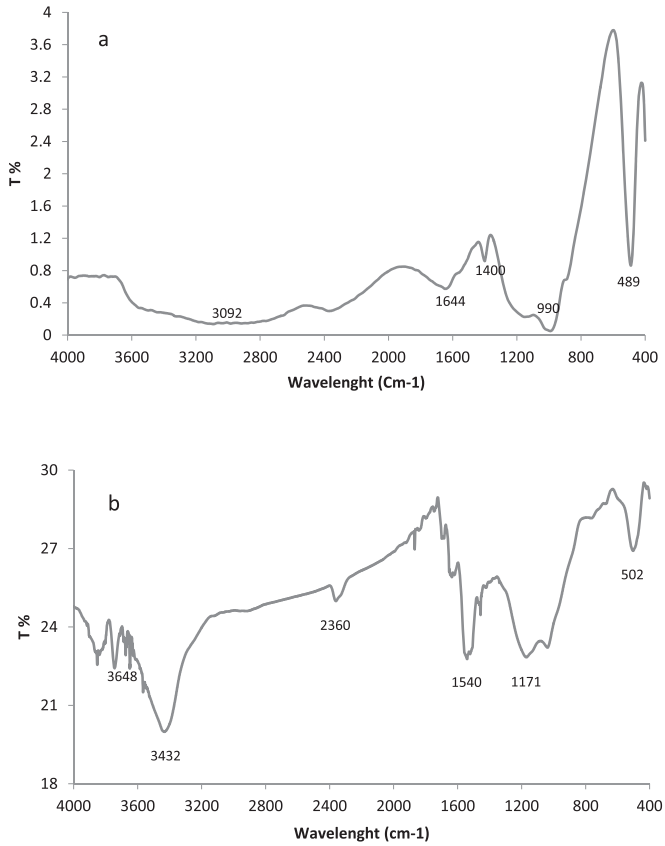

Figure 3. FTIR spectra of PPC(a) and PPAC(b).

development of large bubbles in the solution. Once these large bubbles explode and intense thermodynamic conditions develop, some streams with great rates develop in the liquid, thereby causing development of roughness and large pores across the surface of the adsorbent present in the solution [31]. Undeniably, since ultrasonic waves move longitudinally in liquid environments, they create periodic phases of contraction and expansion and at a point where the density is greater, they generate larger pressure and vice versa. This difference in pressure results in development of gas bubbles in the solution. As this trend continues, the formed bubbles attain their maximum volume, and eventually exclusion of bubbles occurs intensively. This explosion of bubbles leads to creation of a very high temperature or hotspots as well as a high pressure in the solution's environment, thereby resulting to intense turbulence in the fluid and the development of sheer force across the adsorbent's surface. This culminates in the development of large pores across the adsorbent surface [32, 33].

The FTIR spectra for PPC and PPAC are shown in figure 3. The most important bands in PPAC have been developed at 3648 and 3432 cm^{-1}, suggesting liberated and bonded (–OH) hydroxyl [34, 35]. The next band has been developed at 2360 cm^{-1}, which is related to C–H groups [36]. Further, the peak at 1540 cm^{-1} represents C–CH_2 and C–CH_3 groups [37, 38]. The peak at 1171 and 502 cm^{-1} can suggest the presence of carbonyl group (C–O) onto the adsorbents, which can be attributed to alcohols, phenols, acids, and other esters [39, 40]. Comparison of the peaks developed for PPC and PPAC indicates that following the activation, OH groups have been developed onto the adsorbent's surface. Studies have shown that MB has a great affinity for OH groups [41]. Therefore, the removal efficiency dramatically grows and shows that the adsorption is both physical and chemical as well.

3.2. Adsorption isotherms

Studying the adsorption isotherms provides us with information about the properties of the adsorbent's surface, the adsorption behavior, and the design of adsorption systems [4]. Moreover, the proportion between the isotherm models and experimental data provides us with information regarding the characteristics of adsorption process [42]. The adsorption data of MB by PPAC at pH = 8, equilibrium time 80 min and 25 °C was matched against Freundlich and Langmuir models (figure 4). In Langmuir isotherm, it is assumed that the adsorption onto the adsorbent is monolayer and all adsorption sites are homogeneous [43]. For Langmuir isotherm, its linear equation (equation (1)) has been used.

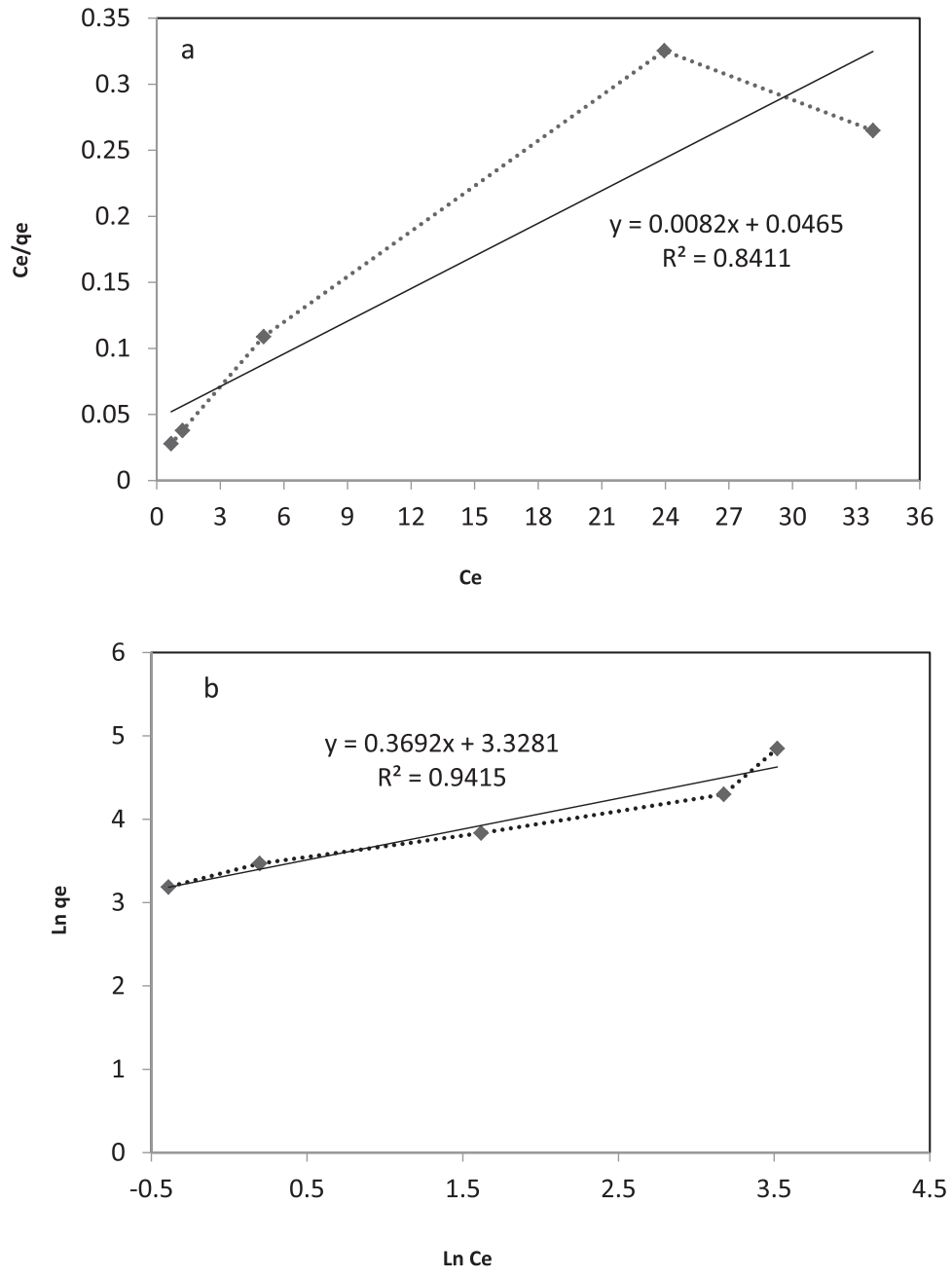

Figure 4. The Langmuir (a) and Freundlich (b) isotherms for MB adsorption on PPAC.

$$\text{Langmuir: } \frac{Ce}{qe} = \frac{1}{Kl^{*}q\ \max} + \frac{C_e}{q\ \max} \tag{1}$$

where, C_e is the final concentration of methylene blue(mg/l) and q_e is the amount of MB absorbed per unit weight of the adsorbent (mg g^{-1}). K_L is the Langmuir constant (L mg^{-1}) which expresses the adsorption of energy. K_L and q_{max} can be obtained out of the diagram's slope and the intersection line of the linear diagram of C_e/q_e versus C_e. The reversibility factor which is associated with Langmuir isotherm and applied for evaluation of the viability of adsorption onto the adsorbent is calculated by equation (2) [44].

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

where, if R_L is equal to zero, it suggests that the adsorption is irreversible. If it is between 0 and 1, then the adsorption is desirable, and if it is equal to 1, then the adsorption is linear. Finally, if it is greater than 1, the adsorption is undesirable. In this study, R_L for adsorption of MB onto PPAC was between 0.0185 and 0.1020 (table 1), suggesting the desirability of MB adsorption [4, 44].

Table 1. Langmuir and Freundlich isotherm parameters for the adsorption of methylene blue on PPAC.

Isotherm	Parameter	R^2
Langmuir	$K_L = 0.176\ L\ mg^{-1}$ $q_{max} = 121.95\ mg\ g^{-1}$	0.8411
Freundlich	$K_f = 27.88\ L\ mg^{-1}$ $n = 2.7$	0.9415

Table 2. Comparison of adsorption capacity of methylene blue onto various adsorbents.

Adsorbent	Maximum adsorption capacity (mg/g)	References
Ultra Sonic Modify–chitin	26.69	[24]
Activated carbon from Coconut coir	15.59	[47]
Commercial activated carbon	14	[48]
Chitosan	30.1	[49]
Coir pit carbon	5.87	[50]
Mesoporous materials synthesized using waste quartz sand	96.9	[51]
Palm tree-activated carbon	90.9	[52]
Waste tea	85.2	[53]
Carbon nanotubes	30	[54]
Halloysite nanotubes	84.32	[55]
PPAC	121.95	This Study

In Freundlich isotherm, the adsorption process takes place in a multilayer form onto the heterogeneous surface of the adsorbent [45, 46]. For Freundlich isotherm, its linear equation (equation (3)) has been used:

$$\text{Freundlich:}\ \ln qe = \ln K_f + \frac{1}{n} \ln Ce \tag{3}$$

where, K_f represents the maximum adsorption capacity ($mg\ g^{-1}$) and 1/n denotes the adsorption intensity and the factor of the degree of heterogeneity. If 1/n is lower than 1, then the Freundlich isotherm is desirable. On the other hand, if 1/n is greater than 1, then it is cooperative adsorption [22]. K_f and n are obtained via the intersection line and the slope of the linear diagram between $\ln q_e$ versus $\ln C_e$ [46].

The parameters related to each isotherm are shown in table 1. The best model was chosen according to determination coefficient or R^2. Accordingly, Freundlich isotherm with a larger R^2 is considered the best model for explaining the adsorption behavior of MB onto the PPAC adsorbent (figure 4). It also shows that the adsorption process takes place in a multilayer form and heterogeneously onto the adsorbent's surface. Moreover, as 1/n is lower than 1, it suggests that the adsorption process of MB onto PPAC has been performed desirably. Moreover, the closer the value of 1/n to zero, the more the adsorption process becomes heterogeneous in nature [36]. So, it can be stated that the heterogeneous surfaces and pores developed through the ultrasonic process are responsible for the adsorption of MB. The results indicate that the PPAC produced in this study possessed a high adsorption capacity when compared with the other adsorbents used for absorbing MB in previous studies as presented in table 2.

3.3. Adsorption kinetics

The adsorption kinetics is one of the most essential parameters for evaluating the efficiency of adsorption process. The two most common models in the evaluation are pseudo-first-order [56] and pseudo-second-order [57] kinetic models. In this study, these models were employed at a temperature of 25 °C and pH of 8 in order to evaluate the MB adsorption process by PPAC.

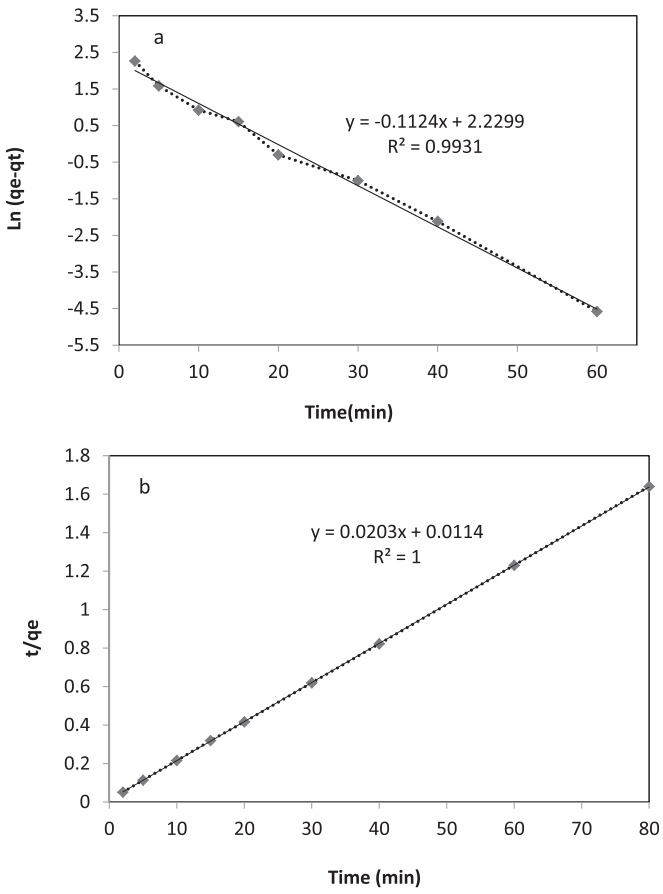

Figure 5. The Pseudo-first order (a) and Pseudo-second order (b) kinetics for adsorption of MB on PPAC.

Table 3. Pseudo-first order and Pseudo-second order kinetic constants for the adsorption of methylene blue on PPAC.

Models	Model parameters	R^2
Pseudo-first order	qe = 9.29 mg g^{-1}	0.9931
	K_1 = 0.1124 min^{-1}	
Pseudo-second order	qe = 49.26 mg g^{-1}	1

The linear form of the pseudo-first-order model is calculated by equation (4).

$$\text{Psedo-first order equation: } \ln(qe - qt) = \ln qe - K_1 t \tag{4}$$

where, q_e (mg g^{-1}) represents the capacity of MB adsorption at the time of equilibrium, qt (mg g^{-1}) denotes the amount of adsorption of MB at the time of t, and K_1 (1/min) shows the constant of the pseudo-first-order rate. The values of K_1 and qe can be calculated via the slope and intersection line of the linear diagram of ln (qe–qt) versus t [4].

The linear form of the pseudo-second order model is calculated through equation (5).

$$\text{Psedo-second order equation: } \frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \tag{5}$$

where K_2 (mg g^{-1}.min) represents the constant of the pseudo-second order rate. The values of qe (1/slope) and K_2 (slope/intercept) can be calculated from t/qt versus t in the diagram [4].

The parameters calculated for the MB adsorption kinetic models by PPAC are provided in table 3. According to the value of coefficient of determination (R^2), the pseudo-second order model has been completely consistent with the experimental results in this study (figure 5). Therefore, it can be stated that, adsorption of MB by PPAC is largely dependent on prisons of sites and pores of adsorption rather than the concentration of the adsorbent in the solution [58]. Furthermore, this model indicates that, chemical adsorption also exists between MB and

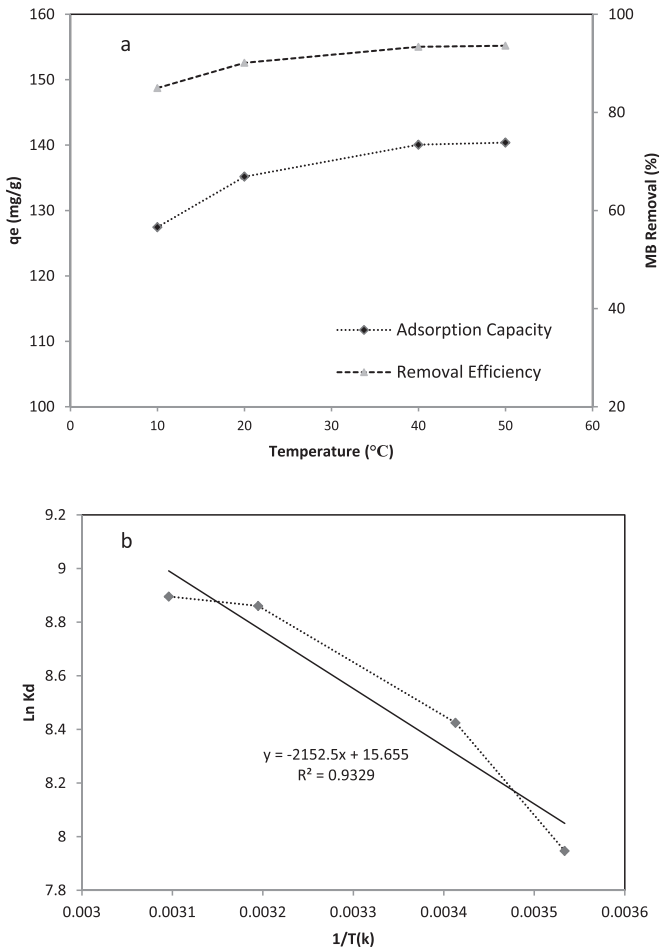

Figure 6. Effect of temperature on adsorption of MB on PPAC (a) and Van't Hoff plot of MB on PPAC for evaluating thermodynamic parameters (b).

PPAC through electron exchange or sharing. Interestingly, results obtained from similar studies performed on the adsorption of MB employing other adsorbents are also consistence with the results in this research [16, 34, 36].

3.4. The adsorption's thermodynamics

The thermodynamic parameters for evaluating the spontaneity trend of the adsorption process are very crucial. These parameters include Gibbs free energy change (ΔG°), enthalpy changes (ΔH°), and entropy changes (ΔS°), and for the adsorption of MB by the PPAC adsorbent, they are calculated using the following formula [59]:

$$K_d = \frac{q_e}{C_e} \times \rho \tag{6}$$

$$\Delta G^\circ = -RTLnK_d \tag{7}$$

$$LnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

Figure 6(a) shows the degree of adsorption of MB by PPAC at various temperatures. The adsorption capacity increased to 140.38 mg g^{-1} when the temperature rose from 10 to 50 °C, with MB removal efficiency growing to 93.38%. It can therefore be stated that the process of methylene adsorption by PPAC is an endothermic process since the adsorption of MB increases with increase in temperature. This can be attributed to the fact that as the temperature rises, the dispersion of MB molecules across the adsorbent's boundary layer increases, the solution's viscosity declines, and the number of collision of MB molecules in the pores of the PPAC adsorbent's surface also increases, culminating in a faster adsorption and more efficient removal [4, 60].

The Van't Hoff plot of MB (figure 6(b)) and calculated thermodynamic parameters are presented in table 4. As can be observed, the value of ΔG° is negative but when temperature was increased, its negative value diminished. This shows that the adsorption process has been carried out easily and spontaneously. It also

Table 4. Thermodynamic parameters for the adsorption of methylene blue on PPAC.

Parameter	Temperature (°k)			
	283	293	313	323
$\Delta G°$ (kJ mol^{-1})	−18.69	−20.52	−23.05	−23.88
$\Delta S°$ (J/mol.k)		130.11		
$\Delta H°$ (kJ mol_{-1})		17.89		
R^2		0.9329		

suggests that the adsorbent PPAC has a great tendency for adsorption of MB from the liquid phase and the adsorption process has been performed better with the elevation of temperature [61, 62]. The studies conducted on $\Delta H°$ in the adsorption process suggest that if $\Delta H°$ is lower than 40 kJ mol^{-1}, then the adsorption process is physical [54]. In this study, since the value of $\Delta H°$ has been 17.89 kJ mol^{-1}, then it can be said that adsorption of MB on PPAC has been mostly physical and the adsorption process has been endothermic which correspondence with the impact of temperature. In addition, positive $\Delta S°$ (130.11 J mol^{-1}.K) represents some changes in the structure of the adsorbent and absorbed compound together with the increase in disorderliness interface between the solid and liquid phase during the adsorption of MB onto the PPAC surface [63, 64]. Indeed, one can therefore infer that the adsorption process in this study takes place physically and in response to electrostatic collisions [36]. This trend of changes in the values of thermodynamic parameters has been similar to the study by Dural *et al* [16], Karacetin *et al* [44], Ma and Wang [34], and Fu *et al* [4] on the adsorption of MB.

3.5. The effect of the solution's pH

The solution's pH can have a significant effect on the adsorption process and the interaction between the adsorbent and absorbed compound [44]. pH_{zpc} for PPAC is 6.3, suggesting that the superficial charges of the adsorbent at this pH is zero. The importance of establishing this point is related to the determination of the adsorbent's surface properties, such that at a pH above the mentioned point, the adsorbent's surface becomes negative, whereby the ions with an opposite charge (positive ions) are easily absorbed. Furthermore, at lower pH, the superficial charges become positive and the ions with a negative charge are adsorbed easily [36]. The effect of initial pH of the solution in MB removal has been shown in figure 7(a). The results indicate that with the increase in pH from 2 to 12, the removal efficiency has increased from 52.46 to 99.46%. This change the PPAC adsorbent behavior in the adsorption of MB but various pH can be associated with pH_{zpc}. Considering the pH_{ZPC}, at pH above 6.3 the adsorbent's surface becomes negatively charged and since the MB dye is a cationic dye, there is thus a better adsorption of the MB molecules onto the PPAC surface [36]. This behavior of pH is in accordance with the study by Dotto *et al* [24], Pirbazari *et al* [41], Li *et al* [65], and Islam *et al* [36].

3.6. The effect of the initial concentration of MB

Figure 7(b) demonstrates the effect of the initial concentration of MB on its removal efficiency. The removal efficiency declined from 99.60 to 74.12% when the concentration of MB increases from 50 to 300. This reduction in the removal efficiency through elevation of initial concentration of MB is caused by restriction of adsorption sites onto the adsorbent's surface. Since the adsorbent's mass is constant across all concentrations, the MB molecules thus tend to compete with each other for adsorption onto the adsorbent's surface, and when the MB's initial concentration increases, the competition becomes more intensive, resulting in decreased removal efficiency [62].

3.7. The effect of mixing rate

The impact of mixing rate in the removal of MB across different rates has been shown in figure 7(c). The results indicate that with the development in mixing rate, the degree of MB removal has also increased, reaching its maximum at around 200 rpm. There is no significant change in the removal efficiency with further rise in missing rate and as a result of this, the optimal rate of 200 rpm has been used in other stages. To express the effect of mixing rate on MB removal, it is safe to infer that, an increase in mixing results in a decline in resistance of boundary layer around the adsorbent surface thereby leading to increase in adsorption levels [66]. Moreover, the extent of collision among MB molecules increases with the growth in mixing rate across the adsorbent, culminating in a faster adsorption.

3.8. The effect of contact time and PPAC dose

The influence of PPAC dose on the degree of MB adsorption across different contact times has been shown in figure 8. The results reveal that the MB's removal efficiency has also grown with the increase in contact time

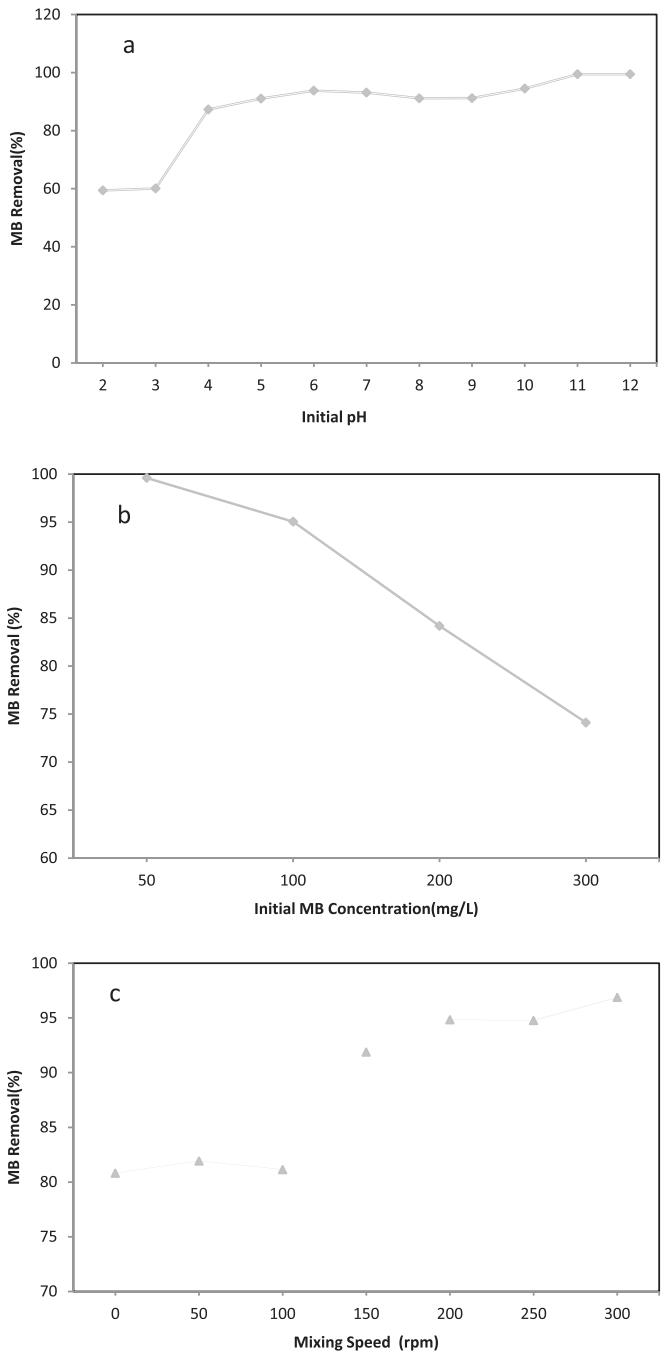

Figure 7. Effects of pH (a) MB initial concentration (b) and mixing speed (c) on the removal of MB by PPAC (initial MB concentration 100 mg l^{-1}, contact time 10 min, PPAC dosage 2 g l^{-1}, pH 8, and mixing speed 200 rpm).

across all doses (0.5-4 g L^{-1}). It can be stated that the free sites of adsorption onto the adsorbent's surface in initial stages are easily accessible to MB molecules [50]. Therefore, when a high concentration of MB is available for adsorption, and the mass transfer at initial contact time increases, the degree of MB's adsorption also rises [62]. Furthermore, figure 8 also demonstrates that with the increase in the adsorbent's dose, MB removal efficiency grows within shorter contact times. As can be observed, at the contact time of 80 min and at the dose of 0.5 and 4 g l^{-1} of PPAC, the removal efficiencies were 83.31 and 99.87%, respectively. Therefore, it can be concluded that increase in MB's removal efficiency with the elevation of PPAC dose is due to the presence of more sites and pores across the adsorbent's surface [67], though there is no significant change in the removal efficiency after the contact time of 80 min at doses above 2 g l^{-1}, and thus the PPAC dose of 2 g l^{-1} has been chosen as the optimal dose. The results of our study are consistent with the results of the study by Moussavi *et al* [62], and Fu *et al* [4].

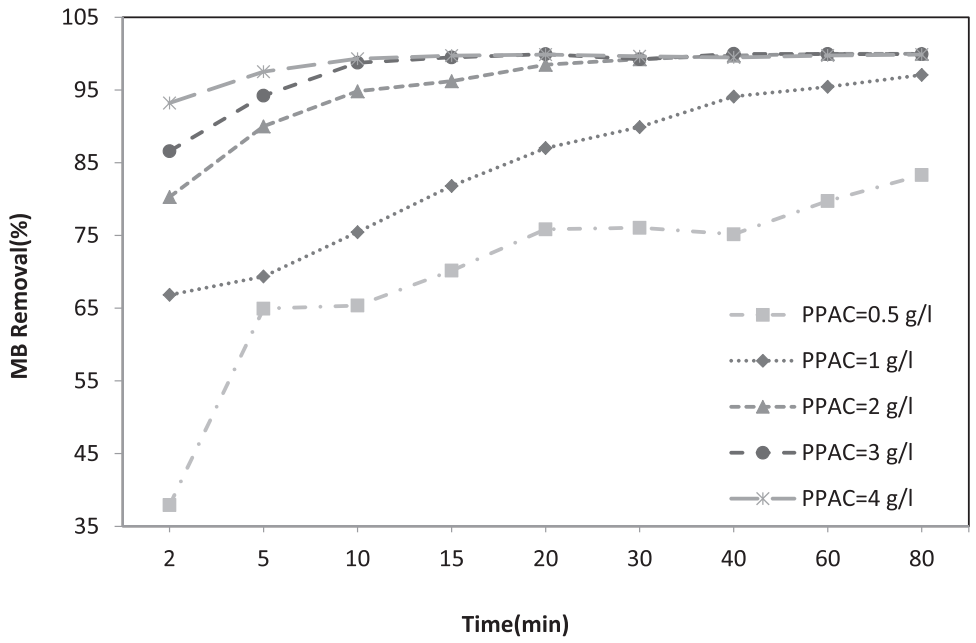

Figure 8. Effect of contact time and PPAC dosage at removal MB by PPAC (pH 8, MB initial concentration 100 mg l^{-1}, contact time 2 to 80 min, PPAC dosage 0.5–4 g l^{-1} and mixing speed 200 rpm).

4. Conclusion

In this study, the effect of ultrasonic waves in the production of activated carbon from *Peganum Harmala* seed has been investigated. This was followed by the evaluation of the efficiency of the produced activated carbon in the adsorption of MB dye. The comparison of PPAC with PPC indicated that the specific surface of PPAC has increased tremendously (570 times). Ultrasonic waves cause the development of very large pores onto the adsorbent's surface and changes in the structure of active sites across the adsorbent's surface, resulting in a dramatic increase in the PPAC efficiency for adsorption of MB. Investigation of the isotherms of adsorption process revealed that Freundlich isotherm is the best model for explaining the MB adsorption behavior onto the PPAC adsorbent and the pseudo-second order is the best kinetic model. The thermodynamic analysis of the adsorption's process showed that adsorption of MB by PPAC is spontaneous, endothermic, and physical and that PPAC is very effective in the adsorption and removal of MB from aquatic environments. Therefore, it can be concluded that ultrasonic waves can be introduced as a suitable and novel alternative for activation of carbon in the process of carbon production.

Acknowledgments

The authors thank Birjand University of Medical Sciences for financial and technical supporting.

Conflicts of interest

The authors declare that they have no conflicts of interest

ORCID iDs

Hadi Eslami https://orcid.org/0000-0001-5137-4764
Rasoul Khosravi https://orcid.org/0000-0003-0202-2353

References

[1] Azhar S Saiful, Liew A Ghaniey, Suhardy D, Hafiz K Farizul and Hatim M D Irfan 2005 Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse *American Journal of Applied Sciences* **2** 1499–503
[2] Yagub Mustafa T, Sen T K, Afroze S and Ang H M 2014 Dye and its removal from aqueous solution by adsorption: A review *Advances in Colloid and Interface Science* **209** 172–84

[3] Yao Y, Xu F, Chen M, Xu Z and Zhu Z 2010 Adsorption behavior of methylene blue on carbon nanotubes *Bioresource Technology* **101** 3040–46
[4] Fu J, Chen Z, Wang M, Liu S, Zhang J, Zhang J, Han R and Xu Q 2015 Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis *Chem. Eng. J.* **259** 53–61
[5] Eslami H, Ehrampoush M H, Esmaeili A, Salmani M H, Ebrahimi A A, Ghaneian M T, Falahzadeh H and Fard R F 2019 Enhanced coagulation process by Fe-Mn bimetal nano-oxides in combination with inorganic polymer coagulants for improving As(V) removal from contaminated water *Journal of Cleaner Production* **208** 384–92
[6] Robinson T, McMullan G, Marchant R and Nigam P 2001 Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative *Bioresour. Technol.* **77** 247–55
[7] Santos S C, Vilar V J and Boaventura R A 2008 Waste metal hydroxide sludge as adsorbent for a reactive dye *J. Hazard. Mater.* **153** 999–1008
[8] Zodi S, Merzouk B, Potier O, Lapicque F and Leclerc J-P 2013 Direct red 81 dye removal by a continuous flow electrocoagulation/flotation reactor *Sep. Purif. Technol.* **108** 215–22
[9] Huang J, Cao Y, Liu Z, Deng Z and Wang W 2012 Application of titanate nanoflowers for dye removal: a comparative study with titanate nanotubes and nanowires *Chem. Eng. J.* **191** 38–44
[10] Oliveira C S and Airoldi C 2014 Pyridine derivative covalently bonded on chitosan pendant chains for textile dye removal *Carbohydr. Polym.* **102** 38–46
[11] Ahmad M A, Ahmad N and Bello O S 2014 Adsorptive removal of malachite green dye using durian seed-based activated carbon *Water Air Soil Pollut.* **225** 1–18
[12] Gupta V 2009 Application of low-cost adsorbents for dye removal–A review *J. Environ. Manage.* **90** 2313–42
[13] Elemen S, Kumbasar E P A and Yapar S 2012 Modeling the adsorption of textile dye on organoclay using an artificial neural network *Dyes Pigm.* **95** 102–11
[14] Zhang P, Wang T, Qian G, Wu D and Frost R L 2014 Removal of methyl orange from aqueous solutions through adsorption by calcium aluminate hydrates *J. Colloid Interface Sci.* **426** 44–7
[15] Demirbas A 2009 Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review *J. Hazard. Mater.* **167** 1–9
[16] Dural M U, Cavas L, Papageorgiou S K and Katsaros F K 2011 Methylene blue adsorption on activated carbon prepared from Posidonia oceanica (L.) dead leaves: Kinetics and equilibrium studies *Chem. Eng. J.* **168** 77–85
[17] Satyawali Y and Balakrishnan M 2007 Removal of color from biomethanated distillery spentwash by treatment with activated carbons *Bioresour. Technol.* **98** 2629–35
[18] Low L W, Teng T T, Rafatullah M, Morad N and Azahari B 2013 Adsorption studies of methylene blue and malachite green from aqueous solutions by pretreated lignocellulosic materials *Sep. Sci. Technol.* **48** 1688–98
[19] Ozer C, Imamoglu M, Turhan Y and Boysan F 2012 Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks *Toxicol. Environ. Chem.* **94** 1283–93
[20] Rafatullah M, Ahmad T, Ghazali A, Sulaiman O, Danish M and Hashim R 2013 Oil palm biomass as a precursor of activated carbons: a review *Crit. Rev. Environ. Sci. Technol.* **43** 1117–61
[21] Rafatullah M, Sulaiman O, Hashim R and Ahmad A 2010 Adsorption of methylene blue on low-cost adsorbents: a review *J. Hazard. Mater.* **177** 70–80
[22] Hameed B, Din A M and Ahmad A 2007 Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies *J. Hazard. Mater.* **141** 819–25
[23] Khosravi R, Fazlzadehdavil M, Barikbin B and Taghizadeh A A 2014 Removal of hexavalent chromium from aqueous solution by granular and powdered Peganum Harmala *Appl. Surf. Sci.* **292** 670–7
[24] Dotto G, Santos J, Rodrigues I, Rosa R, Pavan F and Lima E 2015 Adsorption of Methylene Blue by ultrasonic surface modified chitin *J. Colloid Interface Sci.* **446** 133–40
[25] Liu Q-S, Zheng T, Wang P and Guo L 2010 Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation *Ind. Crops Prod.* **31** 233–8
[26] APHA, WEF 2005 *Standard Methods for the Examination of Water and Wastewater* (Washington, DC, USA: American Public Health Association (APHA))
[27] Leyva-Ramos R, Ocampo-Perez R and Mendoza-Barron J 2012 External mass transfer and hindered diffusion of organic compounds in the adsorption on activated carbon cloth *Chem. Eng. J.* **183** 141–51
[28] Vakili M, Rafatullah M, Salamatinia B, Abdullah A Z, Ibrahim M H, Tan K B, Gholami Z and Amouzgar P 2014 Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review *Carbohydr. Polym.* **113** 115–30
[29] Guarín J R, Moreno-Pirajan J C and Giraldo L 2018 Kinetic study of the bioadsorption of methylene blue on the surface of the biomass obtained from the Algae D. antarctica *Journal of Chemistry* **2018** 2124845
[30] Cardoso N F, Lima E C, Royer B, Bach M V, Dotto G L, Pinto L A and Calvete T 2012 Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents *J. Hazard. Mater.* **241** 146–53
[31] Rooze J, Rebrov E V, Schouten J C and Keurentjes J T 2013 Dissolved gas and ultrasonic cavitation–a review *Ultrason. Sonochem.* **20** 1–11
[32] Chen M-W, You S, Suslick K S and Dlott D D 2014 Hot spots in energetic materials generated by infrared and ultrasound, detected by thermal imaging microscopy *Rev. Sci. Instrum.* **85** 023705
[33] You S, Chen M-W, Dlott D D and Suslick K S 2015 Ultrasonic hammer produces hot spots in solids *Nat. Commun.* **6** 1–8
[34] Ma Q and Wang L 2015 Adsorption of Reactive blue 21 onto functionalized cellulose under ultrasonic pretreatment: Kinetic and equilibrium study *J. Taiwan Inst. Chem. Eng.* **50** 229–35
[35] Moussavi G and Khosravi R 2012 Preparation and characterization of a biochar from pistachio hull biomass and its catalytic potential for ozonation of water recalcitrant contaminants *Bioresour. Technol.* **119** 66–71
[36] Islam M A, Tan I, Benhouria A, Asif M and Hameed B 2015 Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation *Chem. Eng. J.* **270** 187–95
[37] Boonamnuayvitaya V, Sae-ung S and Tanthapanichakoon W 2005 Preparation of activated carbons from coffee residue for the adsorption of formaldehyde *Sep. Purif. Technol.* **42** 159–68
[38] Shen W, Li Z and Liu Y 2008 Surface chemical functional groups modification of porous carbon *Recent Patents on Chemical Engineering* **1** 27–40

[39] Al Sagheer F, Al-Sughayer M, Muslim S and Elsabee M Z 2009 Extraction and characterization of chitin and chitosan from marine sources in Arabian Gulf *Carbohydr. Polym.* **77** 410–9
[40] Bedin K C, Martins A C, Cazetta A L, Pezoti O and Almeida V C 2016 KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue removal *Chem. Eng. J.* **286** 476–84
[41] Pirbazari A E, Saberikhah E, Badrouh M and Emami M S 2014 Alkali treated Foumanat tea waste as an efficient adsorbent for methylene blue adsorption from aqueous solution *Water Resources and Industry* **6** 64–80
[42] Kumar K V, Ramamurthi V and Sivanesan S 2005 Modeling the mechanism involved during the sorption of methylene blue onto fly ash *J. Colloid Interface Sci.* **284** 14–21
[43] Chen L and Bai B 2013 Equilibrium, kinetic, thermodynamic, and *in situ* regeneration studies about methylene blue adsorption by the raspberry-like TiO2@ yeast microspheres *Ind. Eng. Chem. Res.* **52** 15568–77
[44] Karaçetin G, Sivrikaya S and Imamoğlu M 2014 Adsorption of methylene blue from aqueous solutions by activated carbon prepared from hazelnut husk using zinc chloride *J. Anal. Appl. Pyrolysis* **110** 270–6
[45] Altınışık A, Gür E and Seki Y 2010 A natural sorbent, Luffa cylindrica for the removal of a model basic dye *J. Hazard. Mater.* **179** 658–64
[46] El Saliby I, Erdei L, Kim J-H and Shon H K 2013 Adsorption and photocatalytic degradation of methylene blue over hydrogen–titanate nanofibres produced by a peroxide method *Water Res.* **47** 4115–25
[47] Sharma Y C and Upadhyay S N 2009 Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir *Energy & Fuels* **23** 2983–8
[48] Yenisoy-Karakaş S, Aygün A, Güneş M and Tahtasakal E 2004 Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics *Carbon* **42** 477–84
[49] Guo R and Wilson L D 2012 Synthetically engineered chitosan-based materials and their sorption properties with methylene blue in aqueous solution *J. Colloid Interface Sci.* **388** 225–34
[50] Kavitha D and Namasivayam C 2007 Experimental and kinetic studies on methylene blue adsorption by coir pith carbon *Bioresour. Technol.* **98** 14–21
[51] Hong J-M, Lin B, Jiang J-S, Chen B-Y and Chang C-T 2014 Synthesis of pore-expanded mesoporous materials using waste quartz sand and the adsorption effects of methylene blue *J. Ind. Eng. Chem.* **20** 3667–71
[52] Ahmad A, Loh M and Aziz J 2007 Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption *Dyes Pigm.* **75** 263–72
[53] Uddin M T, Islam M A, Mahmud S and Rukanuzzaman M 2009 Adsorptive removal of methylene blue by tea waste *J. Hazard. Mater.* **164** 53–60
[54] Yao Y, Xu F, Chen M, Xu Z and Zhu Z 2010 Adsorption behavior of methylene blue on carbon nanotubes *Bioresour. Technol.* **101** 3040–6
[55] Zhao M and Liu P 2008 Adsorption behavior of methylene blue on halloysite nanotubes *Microporous Mesoporous Mater.* **112** 419–24
[56] Ho Y-S and McKay G 1998 Kinetic models for the sorption of dye from aqueous solution by wood *Process Saf. Environ. Prot.* **76** 183–91
[57] Yuh-Shan H 2004 Citation review of Lagergren kinetic rate equation on adsorption reactions *Scim* **59** 171–7
[58] Rudzinski W and Plazinski W 2009 On the applicability of the pseudo-second order equation to represent the kinetics of adsorption at solid/solution interfaces: a theoretical analysis based on the statistical rate theory *Adsor* **15** 181–92
[59] Buvaneswari N and Kannan C 2011 Plant toxic and non-toxic nature of organic dyes through adsorption mechanism on cellulose surface *J. Hazard. Mater.* **189** 294–300
[60] Nasuha N, Hameed B and Din A T M 2010 Rejected tea as a potential low-cost adsorbent for the removal of methylene blue *J. Hazard. Mater.* **175** 126–32
[61] Auta M and Hameed B 2014 Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue *Chem. Eng. J.* **237** 352–61
[62] Moussavi G and Khosravi R 2011 The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste *Chem. Eng. Res. Des.* **89** 2182–9
[63] Jain S and Jayaram R V 2010 Removal of basic dyes from aqueous solution by low-cost adsorbent: Wood apple shell (Feronia acidissima) *Desalination* **250** 921–7
[64] Liu R-L, Liu Y, Zhou X-Y, Zhang Z-Q, Zhang J and Dang F-Q 2014 Biomass-derived highly porous functional carbon fabricated by using a free-standing template for efficient removal of methylene blue *Bioresour. Technol.* **154** 138–47
[65] Li W-H, Yue Q-Y, Gao B-Y, Ma Z-H, Li Y-J and Zhao H-X 2011 Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions *Chem. Eng. J.* **171** 320–7
[66] Özdemir M, Durmuş Ö, Şahin Ö and Saka C 2015 Removal of methylene blue, methyl violet, rhodamine B, alizarin red, and bromocresol green dyes from aqueous solutions on activated cotton stalks *Desalin. Water Treat.* **57** 1–11
[67] Hameed B 2009 Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent *J. Hazard. Mater.* **162** 344–50