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Mass transfer and thermodynamic analysis on the removal of naphthalene from aqueous solution using oleic acid modified palm shell activated carbon

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ABSTRACT

The present research is focussed on the preparation of palm shell activated carbon by oleic acid (PSAC) modification for naphthalene removal. The characterization of PSAC involved SEM, EDAX, XRD and FTIR analysis. Further, the thermal stability of PSAC was studied using TGA analysis. The studies were further continued to evaluate the optimization parameters such as contact time, pH, temperature, naphthalene concentration and adsorbent dosage. The optimum conditions for the maximum removal of naphthalene for an initial naphthalene concentration of 5 mg/L, solution pH of 2.0, PSAC dosage of 5.0 g/L, contact time of 90 min and the temperature of 30°C. The adsorption kinetics of naphthalene onto PSAC was described by pseudo-first order, pseudo-second order and Elovich models. The equilibrium data were analysed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The Freundlich model provided the best fit of adsorption isotherm for naphthalene by PSAC. The maximum adsorption capacity of PSAC was found to be 44.87 mg/g. The temperature dependence of adsorption process was associated with the changes in several thermodynamic parameters such as Gibbs free energy, enthalpy and entropy. The results suggested that the newly prepared PSAC can act as a promising adsorbent for the removal of naphthalene from aqueous solution.

Keywords: Adsorption mechanism; Naphthalene; Modification; Kinetics; Mass transfer; Thermodynamics

1. Introduction

Poly aromatic hydrocarbons (PAHs) containing two or more than two benzene rings and they are grouped into angular, linear or clustered pattern. They possess hydrophobic nature and non-polar character. They are less water soluble which results in reduced solubility when molecular weight increases [1–2]. PAHs are found in the environment as a combination of various aromatic compounds in which each one has the ability to influence other elements. They are a very influential class of environmental pollutant causing harmful effects to the environment [3]. Poly-aromatic hydrocarbons are organic pollutants, which cause widespread carcinogenic and mutagenic diseases by reacting with DNA. PAHs found application in plastics, dyes and pesticides and in medicine. Hence, they enter into envi-

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ronment through dry and wet depositions in atmosphere, runoff, hydro-carbon spills, water bodies and industrial discharge, especially from processing industries [4]. Anthropogenic activities such as petroleum spillages also led to the maximum disposal of PAHs into the environment. PAHs possess electrochemical stability with high boiling and melting points [5,6]. PAHs possess greater mobility and longer time persistence in the environment. Hence, World Health organization has set up a tolerance limit value for the influence of PAH in potable water available for drin king [7].

Naphthalene was considered one of the most notable PAHs in wastewater [8]. Naphthalene is simple and more volatile, which seems to be less toxic among different PAHs. Naphthalene is excessively observed in wastewater, discharged from various processing plants operated in refineries and petrochemical plants [9,10]. There are various methods available to treat PAHs, which include biodegradation, solvent extraction, liquid-liquid extraction and adsorption [11–14]. Among these, adsorption finds to be economic and cost efficient. Adsorption provides flexibility and simple design, easy operation, and possesses more effectiveness in the removal of naphthalene from the water environment, specifically at lower concentrations [15–17]. Different adsorbents were used in treatment processes are of biological origin, mineral, biomass, agricultural wastes and other industrial byproducts [18–26].

Activated carbon obtained from agricultural waste has proved to be an effective adsorbent due to high surface area, porosity and surface properties [27–31]. Activated carbon finds to be a porous material containing maximum surface area to adsorb the contaminants [32]. Many researchers have done work on activated carbon obtained from agricultural waste materials such as coconut shell, pea nut shell, bagasse, almond shell, saw dust and palm shell. More amount of waste materials are obtained as of agricultural dropouts such as coconut, coir pith, peanut, almond, corn and palm shell [33]. Removal of Naphthalene by adding high surface adsorbing capacity adsorbents is an easy and an efficient way along with reducing cost factor. Hence, the development of adsorbents with maximum adsorption capacity makes the management and reduction of environmental pollution to a great way. Carbonization tends to increase the sorption capacity of activated carbon since it is related to the material surface characteristics [34]. Though few works have been done on palm shell, this work brings the modification of palm shell activated carbon using oleic acid [35]. The present study explains the effect of oleic acid addition onto palm shell activated carbon.

The aim of the present experimental study is to examine the achievability of chemically modified palm shell activated carbon (PSAC) for the adsorption of naphthalene from its aqueous solution. Surface properties of PSAC were characterized by SEM, EDX, XRD, FTIR and TGA analysis. The impacts of the operation parameters on the adsorption process, such as initial naphthalene concentration, biosorbent amount, temperature, contact time, and solution pH, amid the adsorption procedure were also investigated. In order to examine the adsorption behavior of PSAC, adsorption isotherm and kinetic models were fitted with the present equilibrium and kinetic data, respectively.

2. Materials and methods

2.1. Adsorbate

Naphthalene, Oleic acid, butanol was purchased from Sigma Aldrich Chemicals, India. Naphthalene ($C_{10}H_8$), as the delegate compound of PAHs with a sub-atomic weight of 128.16 g/mol, was utilized as a model adsorbate in this research. Because of the low water dissolvability of naphthalene, the water–butanol arrangement was utilized as the fluid arrangement. It is noticed that butanol is a good dissolvable used to improve the adsorption of non polar naphthalene from the hydrophobic condition, framing the naphthalene-containing arrangements. 0.15 g of naphthalene was added into 45 mL of butanol solution. Then, the stock solution was prepared by dissolving the required amount of naphthalene–butanol solution into the deionized water. Since various concentration of naphthalene solutions were required for the present adsorption studies in particular 5–25 mg/L. The pH of each working arrangements was changed in accordance with the required an incentive by utilizing 0.1M NaOH or 0.1N HCl before blending the adsorbent.

2.2. Adsorbent

Palm shells were collected from Vellore, Tamilnadu. The collected biomass was washed using distilled water to remove the impurities present on the surface of the biomass. The biomass material was placed in an oven at 110ºC for 24 h to remove moisture. The dried palm shell was crushed and grinded to fine powder. Then, powdered material was further proceeding for both chemical (oleic acid) and thermal treatment. The resulting material was allowed to dry in an oven at 60°C and then subjected to carbonization for 1 h 30 min at 300°C in a muffle furnace. The subsequent materials were washed by using hot deionized water and the addition of 0.1 mol/L oleic acid in the ratio of 1:3. The excess acid present in the solution was washed until the pH of the supernatant remains constant pH of 7.0. This prepared material is named as palm shell activated carbon (PSAC).

2.3. Characterization studies

The surface morphology of PSAC was explained using Scanning electron microscope, Sem Supra 55 Carl Zeiss, Germany. The elemental composition of adsorbent material was determined using Energy-dispersive X-ray spectroscopy, EA 110 CHN Elemental analyser (Thermo Finnigan model). The presence of important functional groups in PSAC was identified by Fourier transform infrared spectroscopy (FTIR Spectrometer, SHIMADZU, Japan). The crystalline nature of PSAC was determined by X-ray diffraction analysis, Rikagu lab equipment which was maintained at a voltage of 35 kV and a current of 25 MA Cu-Kα2 radiations. The thermal stability of PSAC was estimated by Thermo gravimetric analysis, SDT Q600 V8.0 Build 9.5 Model, TA instruments, USA.

2.4. Batch adsorption studies

Batch experiments were conducted in 250 mL conical flasks in a laboratory shaker at 85 rpm in order to optimize the factor influencing parameters such as initial naphthalene concentration, solution pH, contact time, adsorbent dosage and temperature. In each adsorption tests, the required amount of PSAC was added into the 250 mL of conical flask containing 100 mL of desired concentration of naphthalene solution. The flasks were placed in temperature controlled shaking incubator (Orbitek, India) and agitated at 80 rpm for about different time intervals. After the predetermined time interval, the samples were withdrawn from the incubator and filtered by using Whatman 42 filter paper. The collected supernatant liquid was subjected to UV/Vis analysis using a UV/Vis Spectrophotometer. The percentage removal of naphthalene was calculated from the differences between initial C_o and final concentrations C_e of naphthalene in the aqueous solution during adsorption process.

$$\%\ \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

2.5. Adsorption isotherm study

The adsorption isotherm study was helpful to determine the interaction between the surface of the PSAC and naphthalene in the liquid solution at an equilibrium condition. The batch adsorption study was conducted by varying the naphthalene concentrations varying from 5 to 25 mg/L. In that, required amount of PSAC was added into each conical flask at an optimum condition. Once the framework was accomplished the equilibrium time, the samples were withdrawn from the incubator and filtered by using Whatman 42 filter paper. The collected supernatant liquid was subjected to UV/Vis analysis using a UV/Vis Spectrophotometer. The equilibrium adsorption capacity (q_e) of the PSAC was calculated by using the following formula

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_o is the initial concentration of naphthalene in the solution (mg/L), C_e is the final concentration of naphthalene in the solution (mg/L), V is the volume of naphthalene solution (L) and m is the mass of PSAC (g).

In the present study, adsorption equilibrium data were applied to four different adsorption isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The nonlinear regression analysis was carried out by using MATLAB R2009a software to estimate the isotherm parameters, correlation coefficients (R^2) and error values (SSE and RMSE).

Langmuir isotherm model is given as follows [36]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_m is the maximum mono layer adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant (L/mg).

Freundlich isotherm model is given as follows [37]

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant $[(\text{mg/g})(\text{L/mg})^{1/n}]$ which can be used to measure the adsorption capacity. n is the Freundlich exponent which is used to measure the favorability of the adsorption

Temkin isotherm model is given as follows [38]

$$q_e = \frac{RT}{b}(\ln AC_e) \tag{5}$$

where A and b are the Temkin isotherm constants.

Dubinin-Radushkevich isotherm model is given as follows [39]

$$q_e = q_{m,D} \exp\left[-\beta\left(RT\ln\left(1+\frac{1}{C_e}\right)^2\right)\right] \tag{6}$$

where $q_{m,D}$ is the Dubinin-Radushkevich monolayer adsorption capacity (mg/g) and β is a constant related to adsorption energy.

2.6. Adsorption kinetic study

The adsorption kinetic study can be used to determine the adsorption behavior of present adsorption process at an equilibrium condition. The batch adsorption study was conducted by adding 0.5 g of PSAC in 250 mL of conical flask containing 100 mL of known concentration of naphthalene solution (5–25 mg/L). The solution mixtures were placed in temperature controlled shaking incubator at the temperature of 30°C for about different time intervals (10–120 min). Once the framework was accomplished the equilibrium time, the samples were withdrawn from the incubator and filtered by using Whatman 42 filter paper. The collected supernatant liquid was subjected to UV/Vis analysis using a UV/Vis Spectrophotometer. The amount of naphthalene adsorbed onto the PSAC at an equilibrium time was calculated by using the following formula.

$$q_t = \frac{(C_o - C_t)V}{m} \tag{7}$$

where C_t is the concentration of naphthalene in the solution at time t (mg/L).

Four adsorption kinetic models were used to fitted with adsorption kinetic data. The nonlinear regression analysis was carried out by using MATLAB R2009a software to estimate the kinetic model parameters, correlation coefficients (R^2) and error values (SSE and RMSE).

The pseudo-first-order kinetic model is given as follows [40]

$$q_t = q_e\left[1 - \exp\left(-k_1 t\right)\right] \tag{8}$$

where k_1 is the pseudo-first-order kinetic rate constant (min^{-1}).

The pseudo-second-order kinetic model is given as follows [41].

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

where k_2 is the pseudo-second order kinetic rate constant (g/mg·min).

The Elovich kinetic model is given as follows [42]:

$$q_t = \left(1+\beta_E\right)\ln\left(1+\alpha_E\beta_E t\right) \tag{10}$$

where α_E is the initial adsorption rate (mg/g·min) and β_E is the desorption constant (g/mg) which is related to the activation energy of chemical adsorption.

2.7. Adsorption thermodynamic study

Thermodynamic studies were carried out by adding 0.5 g of PSAC in 100 mL of known concentration of naphthalene solution (5–25 mg/L). The solution mixtures were placed in temperature controlled shaking incubator for different temperatures in the range of 30–60°C at an equilibrium time of 90 min. Once the framework was accomplished the equilibrium time, the samples were withdrawn from the incubator and filtered by using Whatman 42 filter paper. The collected supernatant liquid was subjected to UV/Vis analysis using a UV/Vis Spectrophotometer. The thermodynamic behavior can be estimated by fixing the experimental data to the thermodynamic equations. The thermodynamic parameters such as Gibbs free energy (ΔG°), entropy and enthalpy were calculated by using the following formula

$$\Delta G^o = -RT\ln(K_c) \tag{11}$$

$$LogK_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{12}$$

where K_c is the coefficient of distribution which is the ratio of naphthalene concentration on the solid phase and the naphthalene concentration in liquid phase at equilibrium. T is the adsorption system temperature and R is universal gas constant.

3. Results and discussions

3.1. Characterization studies

3.1.1. Fourier transform infrared analysis

FTIR analysis can be used to elucidate the presence of important functional groups on the surface of PSAC. FTIR image of PSAC is shown in Fig. 1a. The FTIR spectra were analysed by attenuated total reflectance within the range of 400–4000 cm^{-1}. The peak value at 3347.50 cm^{-1} shows the presence of acetylenic group frequencies of alkyne C-H stretch. The elongated peak was found at 2921.45 cm^{-1} which represents the presence of vibrational stretching of –OH groups. The broad peak at 1587.78 cm^{-1} confirms the stretching of –CH$_2$ groups. The intense peak vibration at 1164.37 cm^{-1} may correspond to the presence of –NH$_2$ bending vibration. The peak values at 597.41 and 552.51 cm^{-1} is corresponding to the presence of aliphatic organohalogen compound group frequencies of aliphatic iodo compounds C-I stretch. The FTIR analysis results confirms that the presence of different functional groups such as hydroxyl, acetyl and amide might play an important role in the binding process between naphthalene and PSAC adsorbent. The presence of aliphatic iodo compounds plays an imperative role in the adsorption of naphthalene onto PSAC. These aliphatic groups form the covalent bond between the surface of the PSAC and the naphthalene solution. FTIR report confirmed that presence of these functional groups will enhance the adsorption capacity of PSAC for the removal of naphthalene from the aqueous solution.

3.1.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy analysis

SEM analysis can be used to determine the morphological characteristics and surface nature of present adsorbent material (PSAC). SEM images of PSAC with different magnifications of 2500× and 500× was shown in Fig. 1b – (i) and (ii). The particle size, shape and porosity of PSAC was determined. The surface pores of PSAC have been found out which demonstrates that PSAC has uniform distribution. The pores are rough and possess more pores which showed caves in between the structure. The size of the pores range is in between of 15–250 nm that was able to form aggregates and clusters due to the existence of intermolecular forces.

Energy disperse X-ray spectroscopy is used for the determination of elemental composition of PSAC. EDX analysis of PSAC was shown in Fig. 1b – (iii) and the results were shown in Table 1. The rod like appearance indicates carbon and oxygen whereas the structural trend indicates other components like Na and K. the surface appears to be uniform due to the formation of micro pores that formed during the chemical treatment onto palm shell activated carbon. The inclusion of carbon and oxygen confirmed the chemical addition of oleic acid onto the palm shell activated carbon. The percentage of carbon and oxygen was estimated to be 77.35% and 21.72% respectively.

3.1.3. X-Ray diffraction analysis

The crystalline nature of PSAC was determined by XRD analysis. XRD image of PSAC is shown in Fig. 1c – (i). The diffractograms resulted through XRD are quite similar and in better understanding with the pattern of the sample. But few undesirable peaks in the XRD pattern revealed the presence of trace amount of impurity in the sample. XRD confirmed the powder pattern of synthesized activated carbon PSAC under atmospheric conditions. XRD also predicted the particle size of PSAC sample in the value range of 2–3 mm. The XRD results confirming that diffraction index for PSAC were less intense and it has more adsorption sites

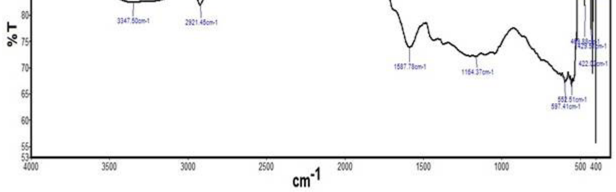

Fig. 1(a). FTIR image of PSAC.

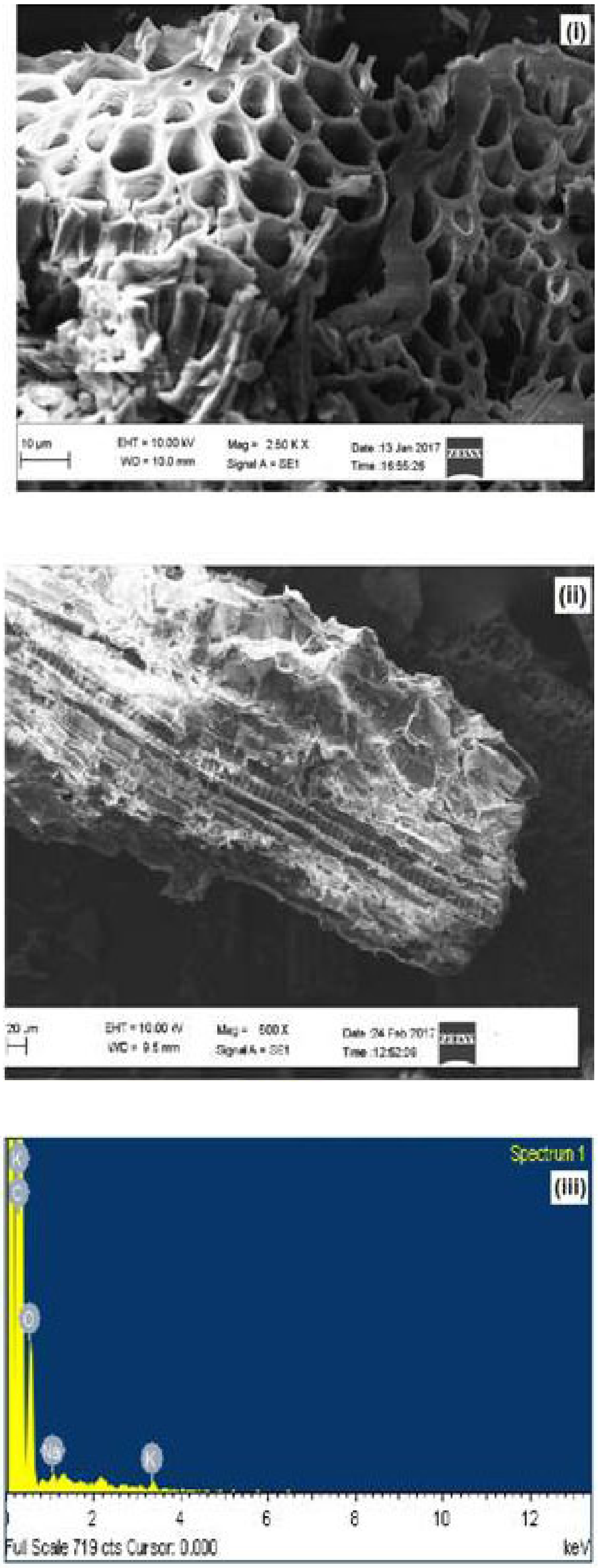

Fig. 1(b). (i) SEM images of PSAC (before adsorption) (ii) SEM images of PSAC (after adsorption) (iii) EDX image of PSAC.

Table 1
Elemental Composition of PSAC

Element	Weight %	Atomic %
C	71.07	77.35
O	26.58	21.72
Na	0.60	0.34
K	1.75	0.59
Total	100	100

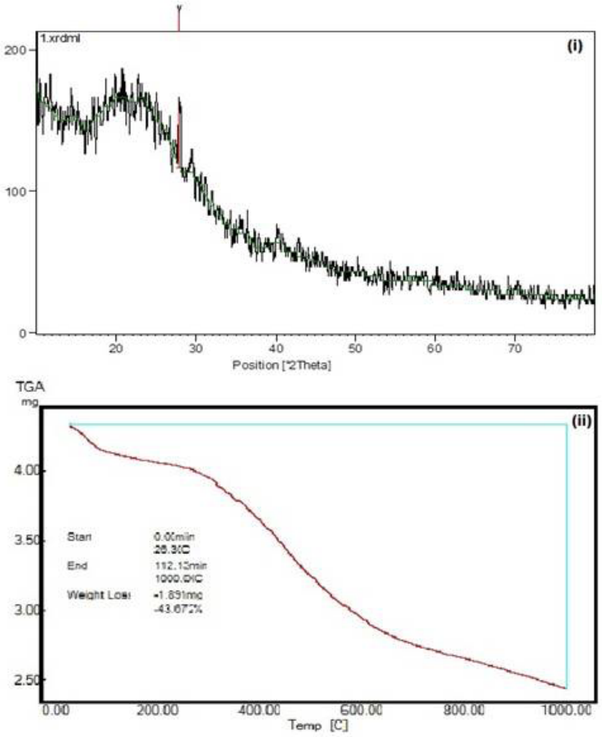

Fig. 1(c). (i) XRD image of PSAC (ii) TGA image of PSAC.

for naphthalene adsorption which may be due to more nebulous structures in it. XRD analysis reported that PSAC has superior capacity for naphthalene adsorption.

3.1.4. Thermo gravimetric analysis

TGA showed that percentage of weight loss of PSAC with respect to experimental conditions. TGA image of PSAC is shown in Fig. 1c – (ii). The two portions formed which indicates that the decomposition of PSAC is taken place at 200°C and this represented nearly 8% of weight lost during the process. This is due to the release of surface moisture by PSAC subjected to heating phenomenon. Major weight loss occurred at a temperature of 400°C–600°C. This is usually represented by the chemical bonding of water molecule with PSAC and the breakdown of various other components such as lignin and cellulose materials decomposition. Continued heating above 600°C results in fall of weight loss which indicated the minimum formation of various carbonaceous gases like CO and CO_2. TGA analysis reported that PSAC infers that the activated carbon is thermally stable between 200–350°C.

3.2. *Effect of pH*

The pH of the naphthalene solution was an important factor during adsorption process which influences the soluble nature of the adsorbate and electrostatic bonding between the adsorbate and adsorbent. The pH of the naphthalene solution was adjusted by using 0.1 N HCl and 0.1 N NaOH. Effect of pH on the adsorption of naphthalene by PSAC was studied by varying the pH in the range of 2.0–8.0 for an initial naphthalene concentration of 5 mg/L, contact time of 90 min and temperature of 30ºC and the result is show in Fig. 2a. The result from Fig. 2a shows that percentage removal of naphthalene was decreased with an increase of solution pH from 2.0 to 8.0. These data could be explained by the variation of the molar fraction of undissociated naphthalene. Generally, activated carbon reacted with undissociated naphthalene by forming hydrogen bonds with hydroxyl groups. However most phenolic compounds act like weak acids in aqueous solution. At low pH, due to the high electrostatic force of desirability, the percentage removal of naphthalene is high. Effect of pH studies showed that maximum removal of naphthalene was observed at the pH of 2.0. Point of zero charge (pH_{pzc}) of the adsorbent material is another parameter to explain the influence of solution pH on the removal of napthalene by the adsorbent. pH_{pzc} of the adsorbent material was found to be below 2.0 which indicates that the adsorbent surface acquired positive charge below this pH value. At solution pH < pH_{pzc}, most of the PAHs will be positively charged which indicates the removal of napthalene below pH_{pzc} value is an ion exchange process. If the solution pH was increased above the pHpzc of the adsorbent then the adsorption process was decreased in the removal of napthalene. After particular pH, the charge on the napthalene species and the adsorbent surface becomes negatively charged which indicates that the adsorption process decreased significantly. For the present adsorption system, the optimum pH was fixed as 2.0 and it was maintained for further experimental studies.

3.3. *Effect of adsorbent dosage*

Adsorbent dosage is an imperative operating parameter to maximize the interaction between the naphthalene in the liquid phase and the adsorptive sites of PSAC in the solid phase. The adsorption capacity of the PSAC was determined by changing the dosage from 1.0 to 7.0 g/L, initial naphthalene concentration of 5 mg/L, solution pH of 2.0, contact time of 90 min and temperature of 30ºC and the experimental data are represented in Fig. 2b. It is observed from Fig. 2b, the percentage removal of naphthalene was increased with an increase of adsorbent dosage from 1.0 to 7.0 g/L. The reason for this behaviour might be due to the increase in available adsorptive sites of the PSAC with an increase of PSAC dosage. It is clear that, maximum percentage removal was attained at 5.0 g/L. Beyond that limit (5.0 g/L), the percentage removal remains fairly constant, this may be due to gradual decrease of available adsorptive sites, low driving force and low equilibrium concentration. The equilibrium adsorption capacity (q_e) was decreased with an increase of PSAC dosage. It might be possibly due to availability of more adsorptive sites and rise in the surface area at lower dosage. At higher adsorbent amount, the reason of the decrease in adsorption amount of naphthalene is that "the higher adsorbent amount leads to a decrease in total surface area by agglomeration and to formation of unsaturated adsorption sites". Consequently, the adsorption amount of naphthalene is higher at lower dosage and overlying of adsorptive sites at higher dosage.

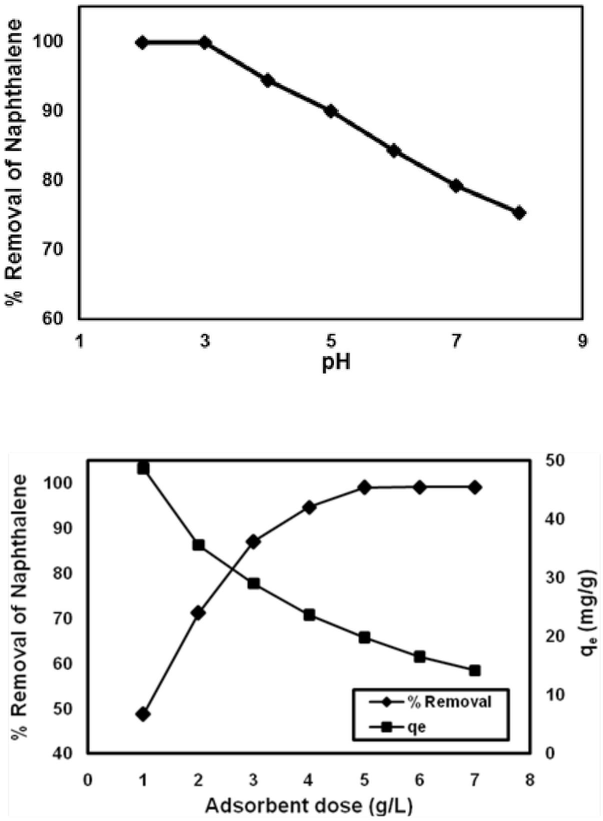

Fig. 2(a). Effect of pH on the adsorption of naphthalene by PSAC, (b). Effect of adsorbent dosage on the adsorption of naphthalene by PSAC.

3.4. *Effect of naphthalene concentration*

The initial naphthalene concentration in the liquid phase plays a significant role, may affects the adsorption process. The effect of naphthalene concentration on the adsorption of naphthalene was carried out by varying the naphthalene concentration in the range of 5–25 mg/L, solution pH of 2.0, PSAC dosage of 0.5 g, contact time of 90 min and temperature of 30°C and the experimental results are shown in Fig. 3a. It is observed from Fig. 3a that the percentage removal of naphthalene was decreased with an increase initial naphthalene concentration from 5 mg/L to 25 mg/L. At lower concentration, the ratio of available adsorptive sites to the naphthalene concentration was higher. Therefore, the removal percentage of naphthalene was high. In the opposition of, at higher concentration, the available adsorptive sites were saturated. Hence, the ratio of available adsorptive sites to the naphthalene concentration was low. The equilibrium adsorption capacity (q_e) of PSAC was increased with an increase of initial naphthalene concentration which may be due to utilization of all adsorptive sites and higher adsorption rate for the adsorption at higher naphthalene concentration.

3.5. Adsorption isotherm study

The general information about the adsorption capacity of PSAC and the characteristics of the adsorption process can be determined by adsorption isotherm study. In this study, four adsorption isotherm model such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich model was used for adsorption isotherm study. The adsorption isotherm study was performed by using the experimental data obtained from the effect of initial naphthalene concentration studies. Fig. 3b shows that adsorption isotherm study on the adsorption of naphthalene by PSAC. The adsorption isotherm parameters, correlation coefficient values, sum of error values [SSE and RMSE] are listed in Table 2. The best fitted adsorption isotherm model can be determined based on higher correlation coefficient value and lower error values. It is observed from Table 2 that the Freundlich isotherm model has higher R^2 value compared to other isotherm models, which was found to be best fitted for the adsorption of naphthalene onto PSAC. The Freundlich isotherm model describes that present adsorption process is heterogeneous in nature. The intensity of adsorption can be described by the Freundlich exponent (n). In this study, n value was found to be 3.048. The n value was greater than unity, which indicates the favourable adsorption of naphthalene by PSAC.

3.6. Effect of contact time

The contact time between the naphthalene in the liquid phase and the surface of the PSAC in the solid phase is a significant parameter for the adsorption process. The effect of contact time for the adsorption of naphthalene onto PSAC was studied by varying the contact time from 10 to 120 min, initial naphthalene concentration of 5 mg/L, solution pH of 2.0, PSAC dosage 0.5 g and temperature of 30°C and the experimental results are shown in Fig. 4a. It can be seen from

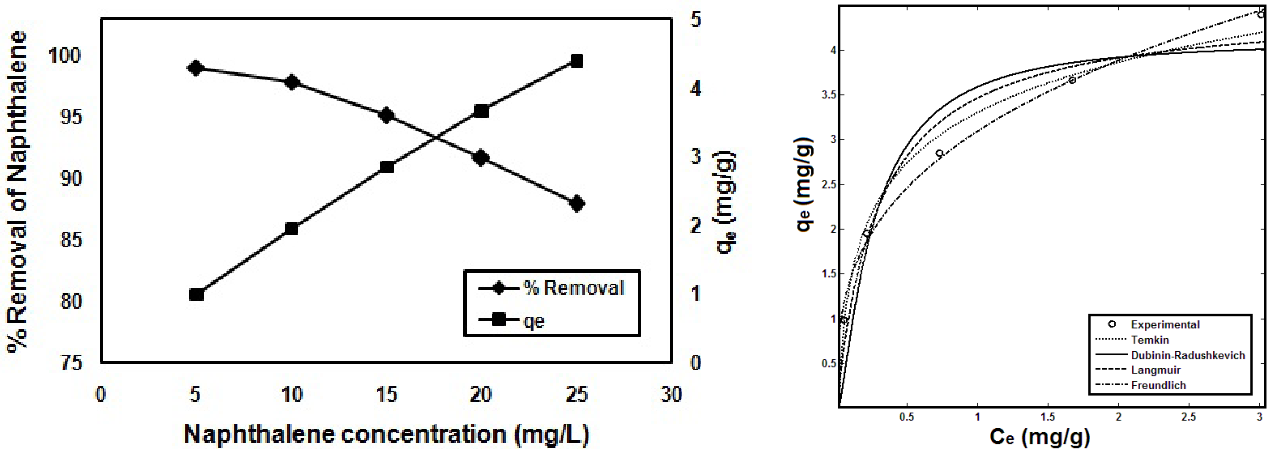

Fig. 3(a). Effect of naphthalene concentration on the adsorption of naphthalene by PSAC, (b). Adsorption isotherm study on the adsorption of naphthalene by PSAC.

Table 2
Adsorption isotherm study on the adsorption of naphthalene by PSAC

S.No	Isotherm model	Parameter	R^2	SSE	RMSE
1.	Langmuir	q_m (mg/g) = 4.487 K_L (L/mg) = 3.379	0.9494	36.86	3.505
2.	Freundlich	K_F ((mg/g)(L/mg)$^{(1/n)}$) = 3.092 n = 3.048	0.9945	4.027	1.159
3.	Temkin	A = 5.93 B = 3.511	0.9852	10.77	1.895
4.	Dubinin-Radushkevich	$q_{m,D}$ (mg/g) = 4.097 b = 8.221 x 10^{-9}	0.8722	0.9309	0.4824

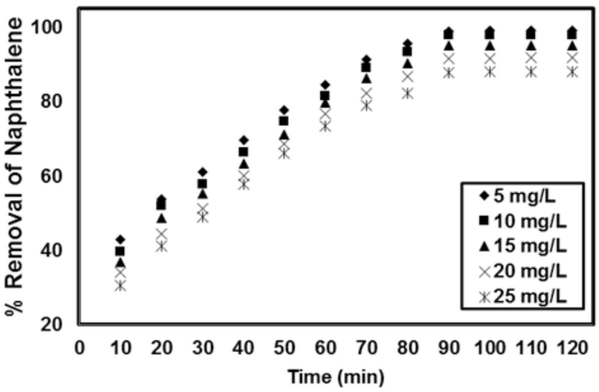

Fig. 4(a). Effect of contact time on the adsorption of naphthalene by PSAC.

Fig. 4a that the percentage removal of naphthalene was highly increased at the initial stage of contact time and attained the maximum percentage removal at 90 min. The reason is initially more number of adsorptive sites were available on the surface of the PSAC. Beyond the contact time of 90 min, the percentage removal remains constant and reaches the equilibrium which may be due to destabilization of driving force and the adsorptive forces were gradually tapered.

3.7. Adsorption kinetic study

Adsorption kinetics plays an imperative role in the adsorption process which can be used to determine the adsorption rate of naphthalene form the aqueous solution onto PSAC. The basic qualities of the good adsorbent material can be evaluated by order of adsorption rate kinetics and adsorption kinetic rate constant. In this study, pseudo-first-order, pseudo-second-order and Elovich kinetic model were fitted with adsorption kinetic data obtained from effect of contact time for naphthalene adsorption onto PSAC. The kinetic parameters, correlation coefficient values, sum of error values [SSE and RMSE] were calculated by using the plot of time vs q_t which is shown in Fig. 4b and the results are listed in Table 3. The tabulation report can be used to identify the best fitted kinetic model. It is observed from Table 3 that the pseudo-second-order has higher correlation coefficient values and lower error values [SSE and RMSE] compared to other kinetic models. In addition to that, comparison statement of calculated adsorption capacity ($q_{e, cal}$) and experimental equilibrium adsorption capacity ($q_{e, exp}$) confirming that $q_{e, cal}$ values of pseudo-second-order kinetic were very closer to the $q_{e, exp}$ values. This authorizes that present adsorption system follows the pseudo-second-order kinetic model which describes that adsorption of naphthalene onto PSAC involves chemisorption mechanism and the rate of adsorptive sites occupation is proportional to the square number of unoccupied sites.

3.8. Effect of temperature

The effect of temperature is the important parameter in the adsorption process. The experimental studies were performed at different temperatures in the range of 30–50°C, initial naphthalene concentration of 5 mg/L, solution pH of 2.0, PSAC dosage 0.5 g and contact time of 90 min and the experimental results are shown in Fig. 5a. It is observed from Fig. 5a that the percentage removal of naphthalene was decreased with an increase of temperature from 30 to 60ºC. At higher temperature, surface area of adsorptive sites was reduced, less number of adsorptive sites were available. This corresponds that present adsorption process was exothermic in nature.

3.9. Thermodynamic study

Thermodynamic study can be used to estimate the nature of the adsorption process such as exothermic or endothermic, randomness and spontaneity. The thermodynamic study of naphthalene adsorption onto PSAC is shown in Fig. 5b. The thermodynamic parameters such as Gibbs free energy (ΔG°) were calculated by using Eq. (11). The values of changes in enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept of the plot of ln K_c vs. 1/T. The calculated thermodynamic parameters are listed in Table 4. From the tabulation report, the negative values of Gibbs free energy are confirming that adsorption process was feasible and spontaneous in nature. The significance of Gibbs free energy describes that; the values of Gibbs free energy were obtained between –20 to 0 KJ/mol for all the temperatures which indicating that present adsorption process was physical adsorption. Furthermore, the negative values of enthalpy mentioning that adsorption of naphthalene onto PSAC was exothermic in nature. The reason for this behaviour might be due to the weak adsorptive forces between the naphthalene molecules and the adsorptive sites on the surface of PSAC. The negative values of entropy describe that decreased randomness at the solid/liquid interface during the adsorption process.

3.10. Design of single stage batch adsorber

Single stage batch adsorber was designed to estimate the amount of PSAC needed to treat known concentration of naphthalene with known volume of naphthalene solution. Schematic diagram of single stage batch adsorber is shown in Fig. 6a. The batch adsorber was designed based on the best fitted adsorption isotherm model. The aim of this design is to reduce the concentration of naphthalene from C_o to C_e for a known volume of naphthalene solution (V). Furthermore, the adsorption capacity of PSAC was changed from q_o to q_e.

The mass balance over the schematic diagram is given as follows

$$V\left(C_o - C_1\right) = M\left(q_1 - q_o\right) = Mq_1 \tag{13}$$

At equilibrium conditions $C_1 = C_e$ and $q_1 = q_e$. In this study, Freundlich model is the best fitted isotherm model. Therefore, Freundlich equation was applied to Eq. (13). Eq. (13) can be rearranged as follows:

$$M = \frac{\left(C_o - C_e\right)}{q_e}V = \frac{\left(C_o - C_e\right)V}{K_F C_e^{1/n}} \tag{14}$$

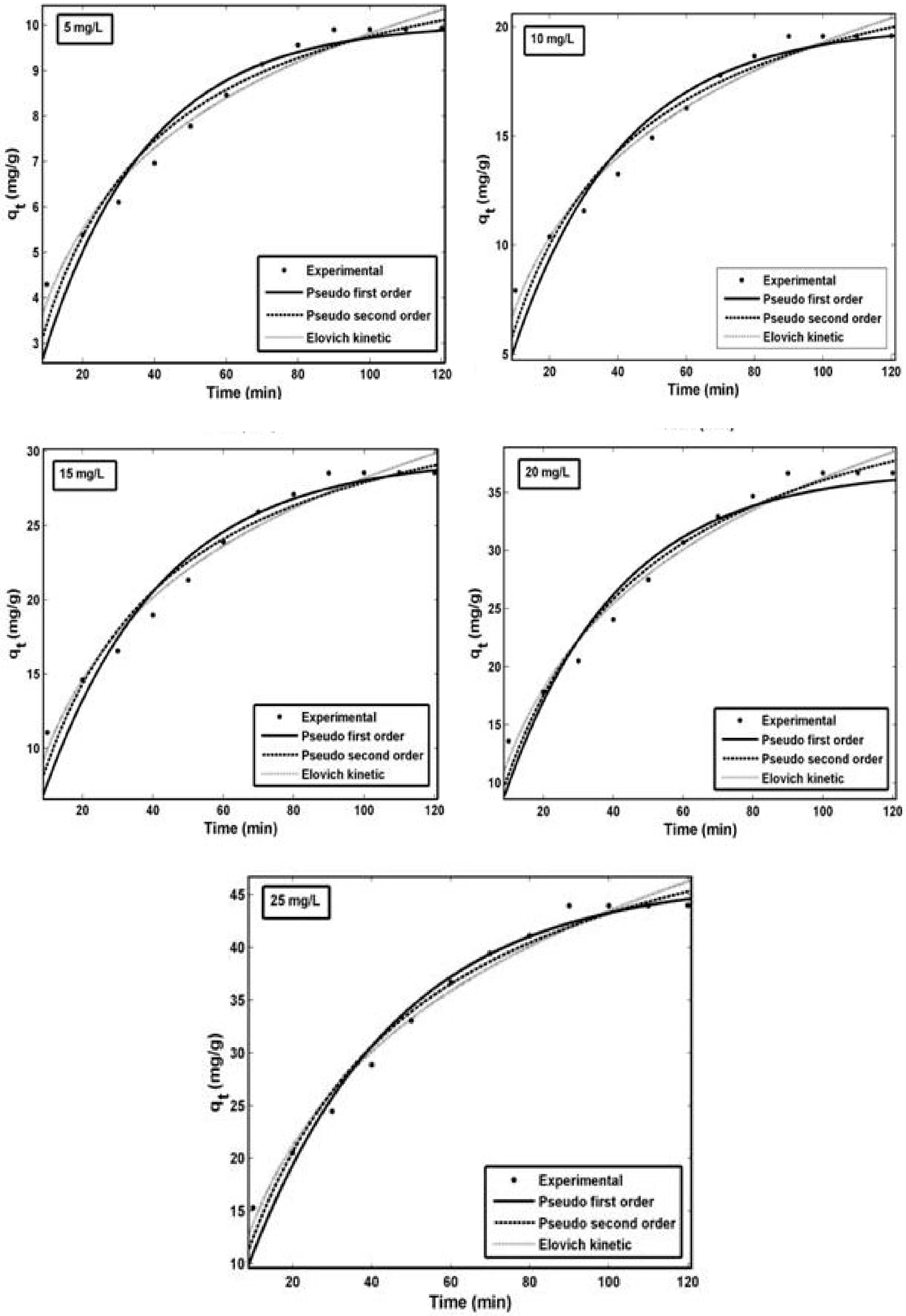

Fig. 4 (b). Adsorption kinetic study on the adsorption of naphthalene by PSAC.

Table 3
Adsorption kinetic study on the adsorption of naphthalene by PSAC

Kinetic model	Parameters	Concentration mg/L				
		5	10	15	20	25
Pseudo first order	k_1 (min^{-1})	0.03459	0.03147	0.0296	0.0308	0.0269
	$q_{e,cal}$ (mg/g)	10.04	20.04	29.55	36.97	46.41
	R^2	0.9329	0.9392	0.9495	0.9552	0.973
	SSE	2.932	11.29	21.33	33.5	30.52
	RMSE	0.5415	1.062	1.46	1.745	1.747
Pseudo second order	k_2 (g/mg/min)	0.0031	0.00134	0.00087	0.00056	0.00044
	$q_{e,cal}$ (mg/g)	12.29	24.95	36.57	48.96	59.63
	$q_{e,exp}$ (mg/g)	12.056	23.586	35.487	46.852	56.811
	R^2	0.9622	0.9631	0.9664	0.9717	0.9796
	SSE	1.65	6.849	14.17	21.16	23.09
	RMSE	0.4062	0.8276	1.135	1.387	1.449
Elovich kinetic	α_E mg/(g·min)	1.231	0.254	0.0251	0.0471	0.0632
	β_E (g/mg)	0.275	1.052	3.785	4.855	6.124
	R^2	0.9601	0.9614	0.9647	0.9708	0.9724
	SSE	1.89	8.25	15.69	28.006	32.56
	RMSE	0.856	0.9110	1.565	2.365	3.085

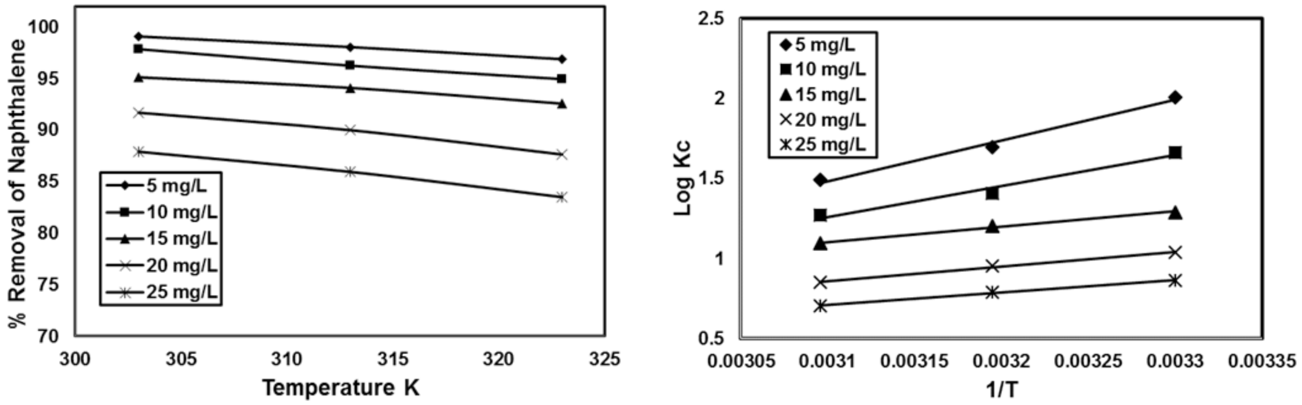

Fig. 5(a). Effect of temperature on the adsorption of naphthalene by PSAC, (b). Thermodynamic study.

Table 4
Thermodynamic parameters for the adsorption of naphthalene by PSAC

Conc of naphthalene solution (mg/L)	(ΔH° kJ mol^{-1})	(ΔS° J mol^{-1}k^{-1})	(ΔG° kJ mol^{-1})		
			30°C	40°C	50 °C
5	–48.595	–122.24	–11.640	–10.146	-9.207
10	–37.066	–90.793	–9.651	–8.441	-7.849
15	–18.147	–38.117	–7.481	–7.205	-6.775
20	–17.713	–35.487	–6.031	–5.708	-5.258
25	–14.772	–32.194	–5.004	–4.720	-4.359

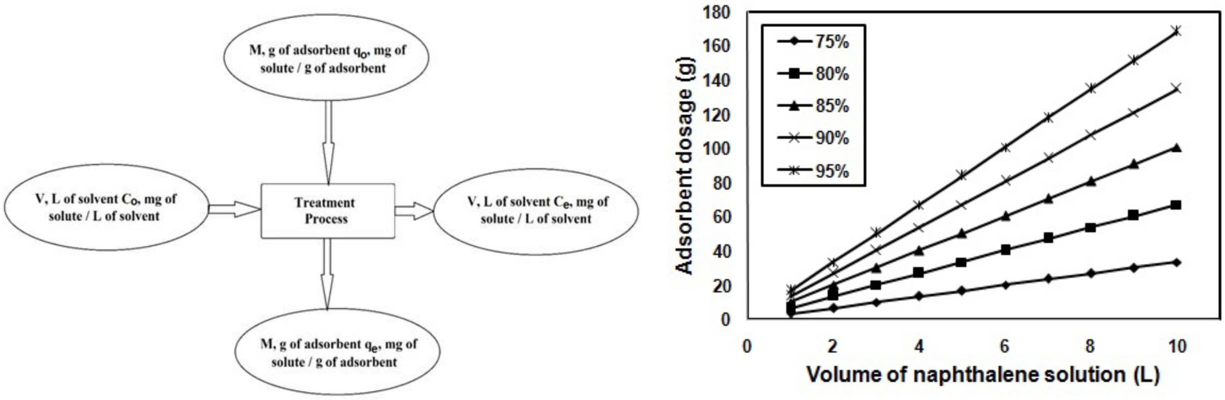

Fig. 6(a). Schematic diagram of a single-stage batch adsorber, (b). Design results of a single-stage batch adsorber.

Table 5
Comparison for the adsorption of naphthalene onto PSAC with various adsorbents

S.No	Adsorbents	q_m (mg/g)	References
1	Waste ion-exchange resins	92.59	[43]
2	Coal based activated carbon	75.76	[44]
3	Zeolite	31	[45]
4	GO/FeOFe$_2$O$_3$	5.72	[46]
5	PSAC	44.87	This study
6	MWCNTs/FeO·Fe$_2$O$_3$	3.56	[46]
7	Graphene oxide	2.62	[47]
8	COMC	2.32	[48]
9	Amberlite XAD-4	0.780	[49]
10	Mesoporous molecular sieves	0.69	[50]

The design results for the single stage adsorber is shown in Fig. 6b. The linear relationship between amount of PSAC and naphthalene solution volume was observed at a naphthalene concentration of 15 mg/L for naphthalene removal ranging from 75 to 95%.

3.11. Performance comparison of the prepared adsorbent

The prepared adsorbent performance was compared with other adsorbents for the removal of naphthalene from aqueous solution and the result is shown in Table 5. The results showed that the prepared adsorbent has an adequate adsorption capacity for naphthalene removal as compared with the other adsorbents.

Declaration

Author's declared that no conflicts of interest for this research article.

4. Conclusion

In this study, adsorption of naphthalene using PSAC was examined under different experimental conditions. The surface modification of palm shell activated carbon was performed by chemical modification using oleic acid. The chemically modified adsorbent material were characterized by SEM, EDAX, XRD, FTIR and TGA analysis. The optimum conditions for the maximum removal of naphthalene by PSAC were observed as follows: initial naphthalene concentration of 5 mg/L, solution pH of 2.0, PSAC dosage of 5.0 g/L, contact time of 90 min and the temperature of 30°C. Comparing the correlation coefficient values reveal that adsorption of naphthalene onto PSAC can be well fitted with Freundlich isotherm model. Adsorption kinetics study reveals that pseudo-second-order model was found to be best fitted to describe the adsorption behaviour. The removal of naphthalene was decreased with an increase in temperature, which indicates that the adsorption of naphthalene onto PSAC was exothermic in nature of adsorption. Thermodynamic studies demonstrated that present adsorption process was feasible and spontaneous in nature. PSAC can supplant as an inexpensive and plentiful carbon source, which will diminish the cost related with overwhelming naphthalene adsorption.

References

[1] P.M. Nacheva, A.E. Sotela, Removal of naphthalene and phenanthrene using aerobic membrane reactor, Biodegradation, 27 (2016) 83–93.

[2] H.I. Abdel-Shafy, M.S.M. Mansour, A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation, Egypt. J. Pet., 25 (2016) 107–123.

[3] P. Issac, F.L. Martinez, N. Bourguignon, L.A. Sanchez, M.A. Ferrero, Improved PAHs removal performance by a defined bacterial consortium of indigenous *Pseudomonas* and actinobacteria from Patagonia, Argentina. Int. Biodeter. Biodegr., 101 (2015) 23–31.

[4] O.S. Ayanda, Occurrence, fate and treatment methods of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins and furans: A mini review, Res. Rev. J Mat. Sci., 2 (2014) 14–21.

[5] Z. Gong, K. Alef, B-M. Wilke, P. Li, Activated carbon adsorption of PAHs from vegetable oil used in soil remediation, J. Hazard. Mater., 143 (2007) 372–378.

[6] S. Bootdee, S. Chantara, T. Prapamontol, Determination of PM$_{2.5}$ and polycyclic aromatic hydrocarbons from incense burning emission at shrine for health risk assessment, Atmos. Pollut. Res. 7 (2016) 680–689.

[7] C.O. Ania, B. Cabal, J.B. Parra, A. Arenillas, B. Arias, J.J. Pis, Naphthalene adsorption on activated carbons using solvents of different polarity, Adsorption. 14 (2008) 343–355.

[8] C.O. Ania, B. Cabal, C. Pevida, A. Arenillas, J.B. Parra, F. Rubiera, J.J. Pis, Effects of activated carbon properties on the adsorption of naphthalene from aqueous solutions, Appl. Surf. Sci., 253 (2007) 5741–5746.

[9] M.A. Barakat, New trends in removing heavy metals from industrial waste water, Arab. J. Chem., 4 (2011) 361–377.

[10] Y.B. Qi, C.Y. Wang, C.Y. Lv, Z.M. Lun, C.G. Zheng, Removal capacities of polycyclic aromatic hydrocarbons (PAHs) by a newly isolated strain from oilfield produced water, Int. J. Environ. Res. Public. Health. 14 (2017) 215.

[11] G. Pinto, A. Pollio, L. Previtera, F. Temussi, Biodegradation of phenols by microalgae, Biotechnol. Lett., 24 (2002) 2047–2051.

[12] J. Shao, Y. Cheng, C. Yang, G. Zeng, W. Liu, P. Jiao, H. He, Efficient removal of naphthalene-2-ol from aqueous solutions by solvent extraction, J. Environ. Sci., 47 (2016) 120–129.

[13] M.S.A. Palma, C. Shibata, J.L. Paiva, M. Zilli, A. Converti, Batch liquid–liquid extraction of phenol from aqueous solutions, Chem. Eng. Technol. 33 (2010) 39–43.

[14] M. Zhu, J. Yao, L. Dong, J. Sun, Adsorption of naphthalene from aqueous solution onto fatty acid modified walnut shells, Chemosphere. 144 (2016) 1639–1645.

[15] L. Gu, H. Guo, P. Zhou, N. Zhu, D. Zhang, H. Yuan, Z. Lou, Enhanced adsorptive removal of naphthalene intermediates from aqueous solution by introducing reed straw into sewage sludge-based activated carbon, Environ. Sci. Pollut. Res. Int., 21 (2014) 2043–2053.

[16] S. Sener, A. Ozyilmaz, Adsorption of naphthalene onto sonicated talc from aqueous solutions, Ultrason. Sonochem., 17 (2010) 932–938.

[17] Q. Shi, A. Li, Z. Zhu, B. Liu, Adsorption of naphthalene onto a high-surface-area carbon from waste ion exchange resin, J. Environ. Sci., 25 (2013) 188–194.

[18] M. El. Haddad, R. Mamouni, N. Saffaj, S. Lazar, Removal of a cationic dye – Basic Red 12 – from aqueous solution by adsorption onto animal bone meal, J. Assn. Arab. Univ. Basic. Appl. Sci., 12 (2012) 48–54.

[19] Shoukat, H.N. Bhatti, M. Iqbal, S. Noreen, Mango stone biocomposite preparation and application for crystal violet adsorption: A mechanistic study, Micropor. Mesopor. Mat., 239 (2017) 180–189.

[20] N. Tahir, H.N. Bhatti, M. Iqbal, S. Noreen, Biopolymers composites with peanut hull waste biomass and application for Crystal Violet adsorption, Int. J. Biol. Macromol., 94 (2017) 210–220.

[21] S. Noreen, H.N. Bhatti, M. Zuber, M. Zahid, M. Asgher, Removal of Actacid Orange-RL Dye Using Biocomposites: Modeling Studies, Pol. J. Environ. Stud., 26 (2017) 2125–2134.

[22] R. Slimani, I. El. Ouahabi, F. Abidi, M. El. Haddad, A. Regti, M.R. Laamari, S. El. Antri, S. Lazar, Calcined eggshells as a new biosorbent to remove basic dye from aqueous solutions: Thermodynamics, kinetics, isotherms and error analysis, J. Taiwan Inst. Chem. Eng., 45 (2014) 1578–1587.

[23] M. El. Haddad, A. Regti, M.R. Laamari, R. Slimani, R. Mamouni, S.El. Antri, S. Lazar, Calcined mussel shells as a new and eco-friendly biosorbent to remove textile dyes from aqueous solutions, J. Taiwan Inst. Chem. Eng., 45 (2014) 533–540.

[24] M. El. Haddad, A. Regti, R. Slimani, S. Lazar, Assessment of the biosorption kinetic and thermodynamic for the removal of safranin dye from aqueous solutions using calcined mussel shells, J. Ind. Eng. Chem., 20 (2014) 717–724.

[25] M. El. Haddad, R. Slimani, R. Mamouni, S. El. Antri, S. Lazar, Removal of two textile dyes from aqueous solutions onto calcined bones, J. Assn. Arab. Univ. Basic. Appl. Sci. 14 (2013) 51–59.

[26] H.N. Bhatti, A. Jabeen, M. Iqbal, S. Noreen, Z. Naseem, Adsorptive behavior of rice bran-based composites for malachite green dye: Isotherm, kinetic and thermodynamic studies, J. Mol. Liq., 237 (2017) 322–333.

[27] A. Ehsan, H.N. Bhatti, M. Iqbal, S. Noreen, Native, acidic pretreated and composite clay efficiency for the adsorption of dicationic dye in aqueous medium, Water Sci. Technol., 75 (2017) 753–764.

[28] V. Tharaneedhar, P.S. Kumar, A. Saravanan, C. Ravikumar, V. Jaikumar, Prediction and interpretation of adsorption parameters for the sequestration of methylene blue dye from aqueous solution using microwave assisted corncob activated carbon, Sustain. Mater. Technol., 11 (2017) 1–11.

[29] P.S. Kumar, A. Saravanan, K.A. Kumar, R. Yashwanth, S. Visvesh, Removal of toxic zinc from water/wastewater using eucalyptus seeds activated carbon: non-linear regression analysis, IET Nanobiotechnol., 10 (2016) 244–253.

[30] S. Anbalagan, S.K. Ponnusamy, S.R.P. Selvam, A. Sankaranarayanan, A. Dutta, Influence of ultrasonication on preparation of novel material for heavy metal removal from wastewater, Korean J. Chem. Eng., 33 (2016) 2716–2731.

[31] A. Saravanan, P.S. Kumar, C.F. Carolin, S. Sivanesan, Enhanced adsorption capacity of biomass through ultrasonication for the removal of toxic cadmium ions from aquatic system: temperature influence on isotherms and kinetics, J. Hazard. Toxic Radioact. Waste, 21 (2017) 04017004.

[32] T. Maneerung, J. Liew, Y. Dai, S. Kawi, C. Chong, C-H. Wang, Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies, Bioresour. Technol., 200 (2016) 350–359.

[33] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review, Bioresour. Technol., 99 (2008) 6017–6027.

[34] S. Valili, G. Siavalas, H.K. Karapanagioti, I.D. Manariotis, K. Christanis, Phenanthrene removal from aqueous solutions using well-characterized, raw, chemically treated, and charred malt spent rootlets, a food industry by-product, J. Environ. Manage., 128 (2013) 252–258.

[35] K.Y. Foo, B.H. Hameed, Utilization of oil palm biodiesel solid residue as renewable sources for preparation of granular activated carbon by microwave induced KOH activation, Bioresour. Technol., 130 (2013) 696–702.

[36] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Amer. Chem. Soc., 40 (1918) 1361–1403.

[37] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.

[38] C. Aharoni, F.C. Tompkins, Kinetics of adsorption and desorption and the Elovich equation, in: D.D. Eley, H. Pines, P.B. Weisz (Eds). Advances in catalysis and related subjects, Academic Press, Newyork (1970) 21–22.

[39] M. Akhtar, S.M. Hasany, M.I. Bhanger, S. Iqbal, Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions, Chemosphere, 66 (2007) 1829–1838.

[40] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungl. Svenska Vetenskapsakad. Handl. 24 (1898) 1–39.

[41] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Proc. Biochem., 34 (1999) 451–465.

[42] M.J.D. Low, Kinetics of chemisorption of gases on solids, Chem. Rev., 60 (1960) 267–312.

[43] C. Long, J. Lu, A. Li, D. Hu, F. Liu, Q. Zhang, Adsorption of naphthalene onto the carbon adsorbent from waste ion exchange resin: Equilibrium and kinetic characteristics, J. Hazard. Mater. 150 (2008) 656–661.

[44] X. Ge, X. Ma, Z. Wu, X. Xiao, Y. Yan, Modification of coal-based activated carbon with nitric acid using microwave radiation for adsorption of phenanthrene and naphthalene, Res. Chem. Intermediat., 41 (2015) 7327–7347.

[45] C.F. Chang, C.Y. Chang, K.H. Chen, W.T. Tsai, J.L. Shie, Y.H. Chen, Adsorption of naphthalene on zeolite from aqueous solution, J. Colloid Interface Sci. 277 (2004) 29–34.

[46] X. Yang, J. Li, T. Wen, X. Ren, Y. Huang, X. Wang, Adsorption of naphthalene and its derivatives on magnetic graphene composites and the mechanism investigation, Colloids Surf. A Physicochem. Eng. Asp., 422 (2013) 118–125.

[47] J. Wang, Z. Chen, B. Chen, Adsorption of polycyclic aromatic hydrocarbons by graphene and graphene oxide nano sheets, Environ. Sci. Technol., 48 (2014) 4817–4825.
[48] M. Anbia, S.E. Moradi, Adsorption of naphthalene-derived compounds from water by chemically oxidized nanoporous carbon, Chem. Eng. J., 148 (2009) 452–458.
[49] C. Long, A. Li, H. Wu, F. Liu, Q. Zhang, Polanyi-based models for the adsorption of naphthalene from aqueous solutions onto nonpolar polymeric adsorbents, J. Colloid Interface Sci., 319 (2008) 12–18.
[50] R.S. Araujo, D.C.S. Azevedo, C.L. Cavalcante Jr, A. Jimenez-Lopez, E. Rodriguez-Castellon, Adsorption of polycyclic aromatic hydrocarbons (PAHs) from isooctane solutions by mesoporous molecular sieves: Influence of the surface acidity, Micropor. Mesopor. Mater., 108 (2008) 213–222.