

Removal of Bromophenols from Wastewater by Sorption

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Poly(ether-block-amide) copolymer (PEBA) was used as an adsorbent for sorptive removal of bromophenols, particularly 4-bromophenol (BP), 2,6-dibromophenol (DBP), and 2,4,6-tribromophenol (TBP) from wastewater. Batch sorption experiments were carried out to examine the bromophenol removal efficiency under different conditions, including temperature, pH, solute concentration, as well as sorbent forms (e.g., size). Both the Langmuir and Freundlich models were fitted to the sorption data well, and the sorption capacities of the three bromophenols were evaluated using the isotherm model. The pseudo-second order kinetics model best fitted the kinetic sorption data, and the rate constants of the phenol sorbates were determined. It was shown that both the internal diffusion and surface “reaction” were important during the sorption process. The activation energies for sorption based on pseudo-second order rate constants were found to be 38.0, 29.7 and 27.7 kJ/mol for BP, DBP and TBP, respectively; while the activation energies based on internal diffusion were 41.7, 32.5 and 28.5 kJ/mol, respectively. The sorption performance of bromophenols on PEBA from industrial effluents related to tetrabromobisphenol A (TBBPA) production was evaluated, and the effects of pH, temperature, phenol concentration, contact time on the bromophenol sorption were investigated. The potential use of PEBA sorbent for treating phenol containing industrial effluents was demonstrated. In addition, regeneration tests of PEBA membrane were performed using deionized water and ethanol (99.5% v/v) as regenerating agents, and the feasibility of reusing the regenerated PEBA membrane in treatment of wastewater from TBBPA industry was confirmed.

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List of Symbols

A	Temperature independent pre-exponential factor
A_I	Adsorbate molecule
$A_I B_I$	Occupied sorption site
B_I	Vacant sorption site
C_e	Sorption equilibrium solution concentration (mmol/L)
C_t	Solution concentration at time t (mmol/L)
C_0	Initial concentration (mmol/L)
C	Intensity of the boundary layer effect (mmol/g)
D_0	Temperature independent pre-exponential factor
D_c	Intra-particle diffusivity (m^2/min)
E_a	Activation energy (kJ/mol)
k	True equilibrium rate constant (L/mmol)
K_H	Henry's sorption constant (L/g)
K_F	Freundlich constant (dimensions are based on n)
K_L	Langmuir constant (L/mmol)

k_1	Pseudo-first order rate constant (min^{-1})
k_2	Pseudo-second order rate constant ($\text{g}/\text{mmol min}$)
k_a	Adsorption rate constant ($\text{L}/\text{mmol min}$)
k_d	Desorption rate constant ($\text{L}/\text{mmol min}$)
k_i	Intra-particle diffusion constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$)
l	Thickness of the sorbent material (m)
M	Mass of PEBA sorbent (g)
N	Number of total potential sites
N_j	Number of occupied sites
n	Factor for system curvature
Q_e	Equilibrium sorption uptake (mmol/g)
Q_m	Maximum sorption capacity (mmol/g)
Q_t	Sorption uptake at time t (mmol/g)
R	Universal gas constant ($\text{kJ}/\text{mol K}$)
t	Time (min)
T	Temperature (K)

V Volume of solution (L)

θ Fraction of adsorption sites covered by adsorbate molecules

Chapter 1

Introduction

1.1 Background

Bromophenol is one of the most important phenol derivatives with bromines, and typical bromophenols include 4-bromophenol, 2,6-dibromophenol, and 2,4,6-tribromophenol.

Bromophenols are classified as organobromines, which are derived from bromine [1]. So far, the content of specific organobromine in seawater is still unclear. However, it is believed that the bromine content in seawater is 65 mg/L, and about 95% of the bromine primarily exists in seawater on the earth [2]. In addition, due to the dynamic biogeochemical cycling, organobromines are the dominant forms of bromine around the globe [3]. Hence, it seems logical that the ocean can be considered as the large natural reservoir of organobromines. In seawater, bromophenols can be found in marine algae, sponges, and worms (e.g., bryozoans), and they are considered as important ocean resources [4]. For example, the simple bromophenols (e.g., 2-bromophenol, 4-bromophenol, 2,4-dibromophenol, 2,6-dibromophenol, and 2,4,6-tribromophenol) from ocean are used in pharmaceutical industry that produces wide varieties of drugs for prophylaxes and treatments of thrombotic diseases [5]. In addition, in the ocean, 2,6-dibromophenol, 2-bromophenol and 2,4,6-tribromophenol are the most strongly flavored compounds with a flavor threshold concentration (FTC) of 5×10^{-4} , 3×10^{-2} , and 0.6 ng/g, respectively, and they can be adsorbed by marine animals from the diet. Hence, bromophenols are identified as the key natural flavor resource of various seafood, such as ocean fish. As organobromines, bromophenols are toxic, and they are considered as chemical defense resources produced by marine organisms [6]. Due to the widespread applications and relative high content in the ocean, enrichment of bromophenols from water is of significant important in utilization of marine resources.

In industries, the aromatic bromophenols are widely applied in the production of fungicides, brominated flame retardant (BFR) and BFR intermediates. In the year of 2001, about 9,500 tons of 2,4,6-tribromophenol was produced in the world. During the production, use, and disposal, bromophenol can be released into soils, aquifers, and groundwater. Meanwhile, like most brominated fire retardants, relative high concentration of bromophenol can cause development of neurotoxicity, embryotoxicity, and fetotoxicity. Due to the potential acute toxicity and endocrine-disrupting

potency, both bromophenol and bromophenol-containing substances are classified as toxic pollutants [7,8]. In 1998, bromophenols were added to the list of hazardous wastes by United States Environmental Protection Agency (USEPA) [9]. For these reasons, pretreatment of wastewater containing bromophenols is necessary in industrial applications [10].

Several techniques have been investigated and developed for the phenolic compound removal and enrichment from water, including adsorption, membrane separation, solvent extraction, bioremediation, and chemical coagulation [11]. Traditionally, adsorption for phenol treatment in water is favored [12]. Adsorption has several advantages, including easy operation in both batch and continuous systems, no sludge formation, and the adsorbent can be regenerated for reuse [13]. Carbon-based materials, which are hydrophobic and non-polar, are the most common and promising sorbent for adsorption separation, even at low concentration. However, for carbon based sorbents, the production process is not environment-friendly, the regeneration process is expensive and complex, and the biodegradability of used sorbents is low [14]. Instead of using carbon based material, polymer based sorbent can be employed as an alternative economic sorbent [15]. Among these novel polymeric sorbents, poly(ether-block-amide) copolymer (PEBA) is demonstrated to have high selectivity for phenols and aromatic compounds in pervaporation process. Due to the presence of electron withdrawing functional groups (amide and ester) and electron donating functional groups (ether) on PEBA chains, bromophenol molecules with electron donating functional groups (bromine and phenol) can interact with the PEBA chain [16]. For this reason, PEBA has been proposed as a convenient sorbent for removal and enrichment of bromophenol from water by sorption process.

Previous studies from our group have explored the potential of using PEBA membrane to remove phenols and mono-substituted phenolic compounds (i.e., 4-chlorophenol, 4-nitrophenol, 4-methylphenol, catechol, and 4-aminophenol) from water. However, detailed work on the sorptive removal of bromophenol and multi-substituted bromophenols from water using PEBA membrane is still lacking [17,18]. This study aims to examine sorption characteristics for 4-bromophenol, 2,6-dibromophenol, and 2,4,6-bromophenol on PEBA sorbents, including sorption isotherms and kinetics. The effects of temperature, initial phenol concentration, pH, processing time, and sorbent on the adsorption performance were investigated.

1.2 Objectives

The objective of this study was to explore the potential of using PEBA sorbent to remove various bromophenols (i.e., 4-bromophenol, 2,6-dibromophenol, and 2,4,6-tribromophenol) from water. The thesis work is composed of the following tasks:

- (1) To perform batch sorption experiments under different conditions (i.e., temperature and initial pH) to study the sorption isotherms.
- (2) To conduct kinetic studies, and the effects of adsorbate concentration, sorbent properties, and temperature on sorption performance were investigated for understanding the sorption mechanisms.
- (3) To confirm the effectiveness of using PEBA membrane for sorptive removal of bromophenols from industrial effluents.
- (4) To perform sorbent regeneration experiments to confirm the potential of reusing PEBA sorbent in treatment of wastewater from tetrabromobisphenol A (TBBPA) industry

1.3 Thesis Outline

The present study consists of six chapters, which are organized and depicted in **Figure 1**.

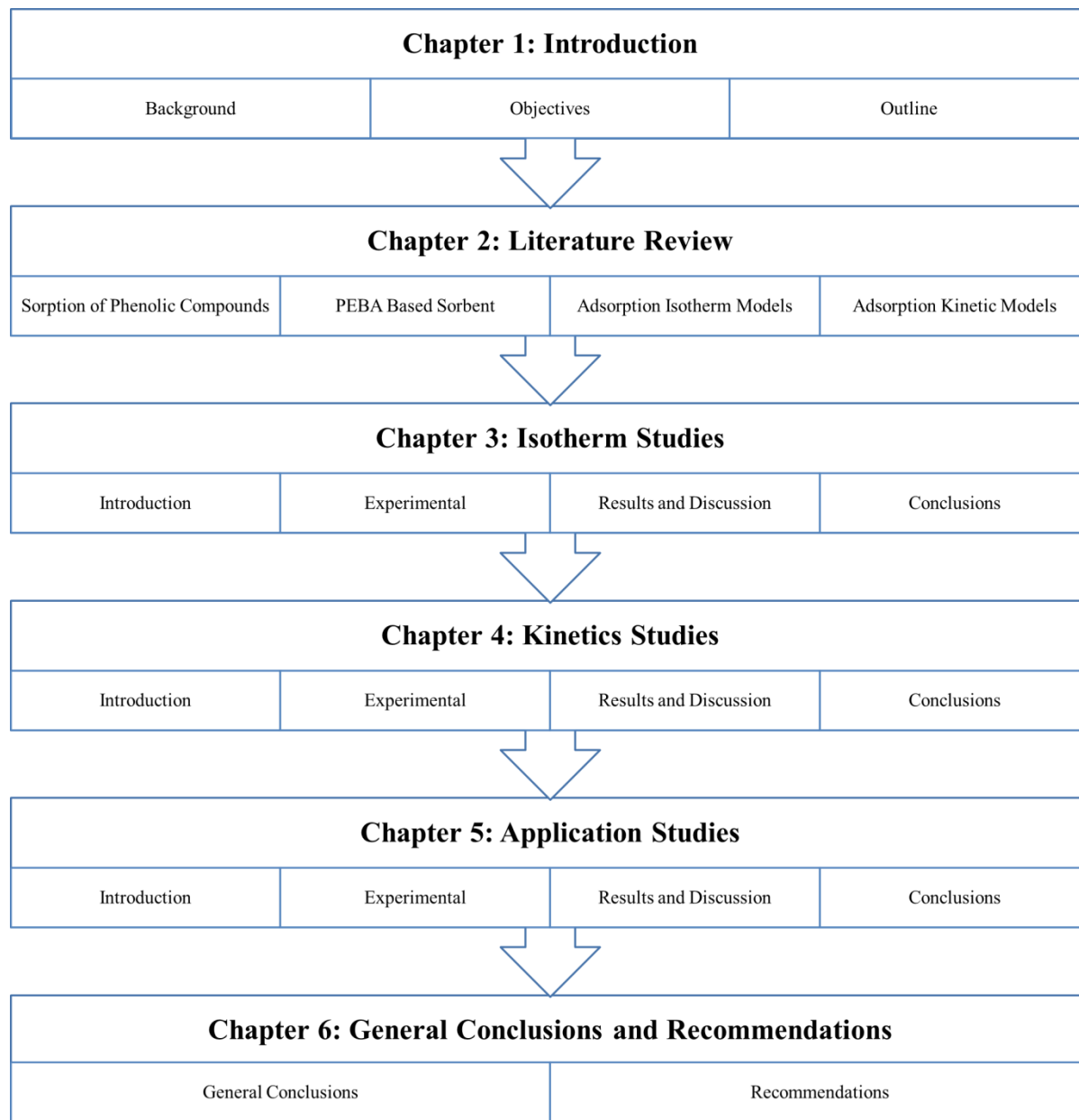


Figure 1 Outline of thesis.

Chapter 2

Literature Review

2.1 Adsorption

Adsorption is a process occurring everywhere in nature. For example, fresh water with large quantities of inorganic and organic gels flows into the sea, and these gels can adsorb various contaminant ions and precipitate in seawater so that the ocean keeps clear blue instead of turning muddy. Meanwhile, with the development of human activity, the precipitated gels accumulate on the river mouth and desorb bad smells, which is a serious problem.

In general, adsorption is defined as the change in density or concentration of a substance from a phase to an interface within solid-gas, solid-liquid, solid-solid, or liquid-gas systems [19]. The substance that accumulates at the interface is called adsorbate, and the substance on which sorption occur is called adsorbent. In general, adsorbates are molecules or ions, which are much smaller than adsorbents, and only a few adsorbates, such as polymeric adsorbents, have similar sizes with adsorbents [20].

Adsorption capacity is an important property of a sorbent. At a given temperature, the relation between adsorption capacity and gas pressure (or liquid concentration) is described by the adsorption isotherm. Adsorption isotherm plots are commonly used to examine the effectiveness of a sorptive separation, and can predict adsorbate/adsorbent interactions (e.g., London dispersion force, electric dipole-dipole interaction, electric quadrupole interaction, and electrostatic force (or Coulomb force)) [21]. More details about adsorption isotherm will be discussed in later sections.

In terms of application, adsorption has been used for separation and purification of gases and liquids a long time ago. In 4000 BC, ancient Egyptians began to use wood and bone char coal to decolor wine, water, and sugar based drinks. In some old Japanese buildings (e.g., Kyoto Imperial Palace), wood char coals are paved under floors to purify the air. Nowadays, adsorption process is widely used in chemical, metallurgic, petroleum, and manufacturing industries.

2.2 Sorptive Removal of Phenolic Compounds from Water

Recently, several sorbents have been studied to remove phenolic compounds from water, including carbonaceous sorbents, mineral based sorbents and polymeric sorbents.

Carbonaceous materials, such as coconut husk, wood, coal etc. can be used to produce various adsorbents by physical or/and chemical activation. The large percentage of micropores, high pore volumes and surface areas, presence of functional groups, and easy modification are typical characteristics of carbonaceous based sorbents, which are responsible for sorptive removal of phenolic compounds [22,23]. While little research has been conducted with sorption of bromophenols onto carbonaceous materials, Bhatnagar [24] has studied the use of carbonaceous sorbents prepared from industrial wastes of fertilizer and steel plants to adsorb 2-bromophenol, 4-bromophenol, and 2,4-dibromophenol. In this study, blast furnace sludge, dust, and slag were also used as sorbents for comparative purpose. It was concluded that the carbonaceous sorbent adsorbed much more bromophenols than other three blast furnace based sorbents. The morphologies of four different sorbents were shown in **Figure 2**.

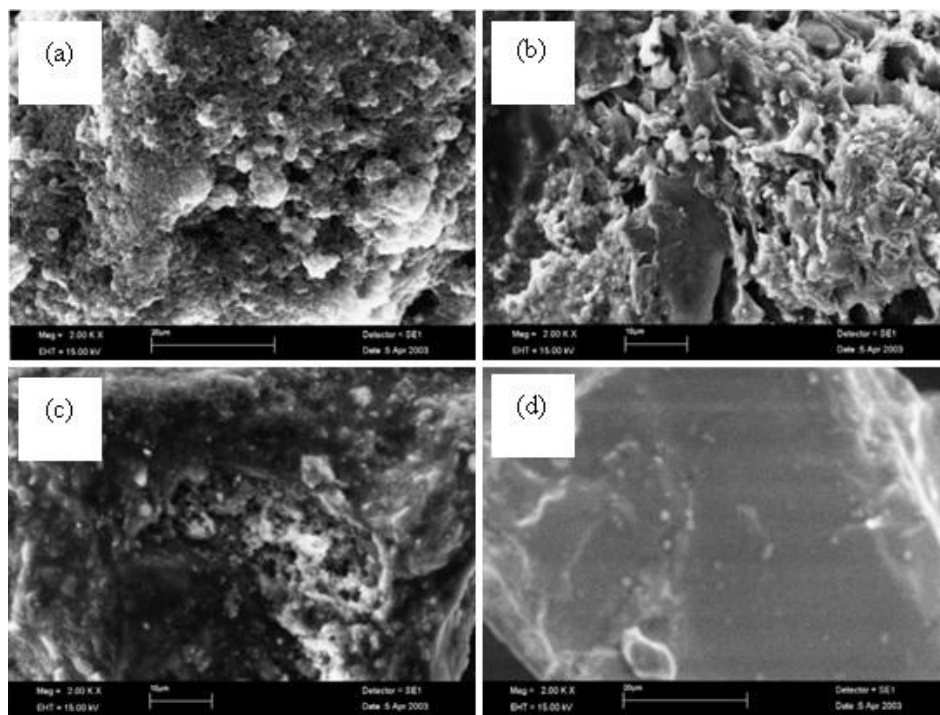


Figure 2 Scanning electron micrograph (SEM) micrographs of carbonaceous sorbents [24].

(a: activated carbonaceous adsorbent; b: activated blast furnace sludge; c: activated blast furnace dust; d: activated blast furnace slag)

It was seen from the micrographs that the carbonaceous based sorbent was highly porous, while the blast furnace based sorbents were not. It was confirmed by SEM micrographs that the carbonaceous based sorbent with a higher porosity leading to a higher surface area was an appropriate material for sorption of various bromophenols [24].

One of the most important commercial carbonaceous products is activated carbon, which shows many positive characteristics for sorption purpose. For instance, the diameter of pores inside coconut shell activated carbon is 10-40 Å, which leads to super high degree of microporosity and surface area. For example, 1 g of activated carbon has a surface area of 1000-1600 m² [25]. Many efforts have been devoted to investigating the feasibility of activated carbon for phenolic compound sorption. For example, Tancredi et al. [26] reported that phenol was preferentially physisorbed onto granular activated carbon prepared from Eucalyptus wood sawdust, and low chemisorbed was detected. Ozkaya et al. [27] reported that the adsorbed phenol remained on the activated carbon and sodium hydroxide had to be used to recover the adsorbed phenol from the sorbent. Ihsanullah et al. [28] reported that the adsorption capacity was significantly affected by the solution pH. Modifying the chemical composition (e.g., oxygen and hydrogen on surface groups) of activated carbon can improve the efficiency of phenolic compound removal. For example, Canizares et al. [29] modified activated carbon Calgon F400 by introducing chloride ions into the activated carbon, which affected significantly its adsorption properties for phenol. Asmaly et al. [30] used ferric oxide to modify the activated carbon surface, so that the phenol adsorption efficiency was enhanced. Abussaud et al. [31] showed Fe₂O₃, Al₂O₃ and TiO₂ nanoparticles-loaded activated carbon had a higher adsorption capacity than raw activated carbon for the adsorption of phenol from water. In spite of the usefulness of activated carbon as an efficient material for phenolic compound sorption, it is still not practically feasible to use activated carbon for the phenol wastewater treatment.

Mineral based sorbents, also known as sinking sorbents, are naturally occurring chemical compounds, and they are fine-grained and high-density materials [32,33]. Mineral based sorbents have been proposed by many researchers as a feasible method for removing phenolic compounds, because of their chemical inertness, non-flammability, easy availability and relative low cost [34-36]. Typical mineral based sorbents include clay and siliceous materials. Clay materials, such as zeolites, kaolinite, and halloysite are considered as the most promising alternatives to activated carbon. Recently, there have been a number of studies devoted to the sorption of phenols using low cost clay sorbents [37,38]. However, most of the clay adsorbents investigated show poor sorption capacity as compared to activated carbons. In addition, there is a risk of dust formation when using clay sorbents

during sorption process in open spaces. Siliceous materials represent a very large group, including silica fume, bentonite, and diatomite, which consist mainly of SiO₂, and some of them are also classified as clay materials, such as bentonite and diatomite. The abundance of siliceous materials in nature and low cost make it a promising sorbent for removal and recycle of many unwanted chemicals from water [39]. Research has shown siliceous materials' ability to bind phenols in water for sorption purpose [40]. For example, Banat et al. [41] reported the potential of bentonite to adsorb phenol from water, and the result revealed that the adsorption capacity of siliceous material-bentonite was increased with phenol concentration and decreased with the pH of the solution. Further study and development of siliceous sorbents for sorption purpose are needed.

2.3 Sorption by Poly(ether-block-amide) Copolymer

Poly (ether block amide) (PEBA) is sometimes called Pebax[®], and it is a block copolymer with the following general chemical structure:

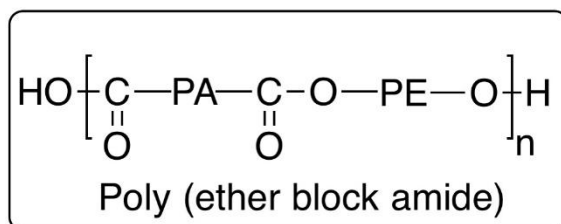


Figure 3 Molecular structure of PEBAX.

PEBA is an important thermoplastic elastomer, where PA represents a group of aliphatic polyamide “hard” blocks (e.g., nylon-6, nylon-12) and PE represents a polyether “soft” block (e.g., poly(ethylene oxide) [PEO], poly(tetramethylene oxide) [PTMEO]). Within the PEBA structure, the PA “hard” component provides the mechanical strength, and the PE “soft” component provides the elastic properties. Increasing PA components in polymer chains leads the elongation of the PEBA to decrease, and the hardness and tensile strength to increase. During the polymerization process, the rigid PA segments with regular linear chains are linked with the flexible PE segments, and the crystalline phase and amorphous phase are combined together to form a copolymer with both thermoplastic and rubber properties.

PEBA has been used widely, including footwear, equipment, and functional films. There has been increasing interest in utilizing PEBA as a material for membranes owing to its excellent chemical, mechanical, and thermal stabilities, and good permselectivity to aromatic compounds and their derivatives. A few studies have shown that PEBA can be a candidate material for separation of

phenolic components from water [42]. Pervaporation of water-phenol by Yahaya revealed the PEBA membranes to be the dominant material with a high selectivity to phenol [16]. Kujawski et al. [43] and Boddeker et al. [44] investigated the pervaporation separation of phenol from water using different grades of PEBA, including PEBAX-2533, PEBAX-4033, and PEBAX-5533.

Among the PEBA category, PEBAX-2533 with 80-86 wt.% poly(tetramethylene oxide) segments is more suitable for effective sorption. PEBAX-2533 is a crystalline polymer, which can be characterized by wide-angle X-ray diffractograms (**Figure 4**).

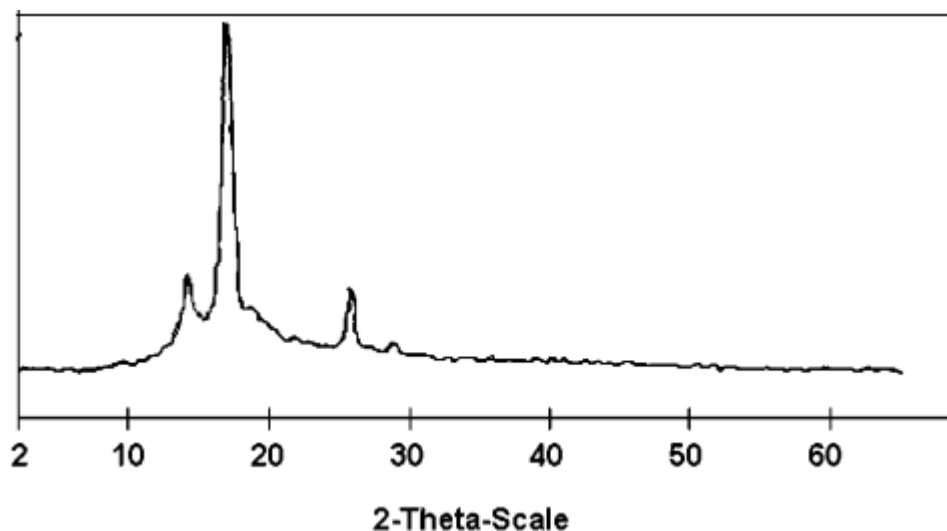


Figure 4 Wide-angle X-ray diffractogram of PEBAX-2533 [45].

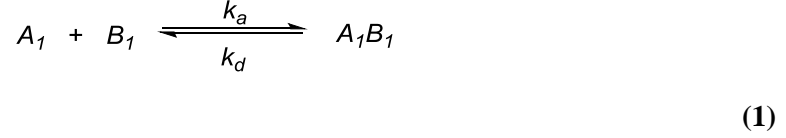
where narrow peaks at $2\theta = 17, 14$ and 26° represent the crystalline region. Various separation studies have demonstrated that the PEBA has excellent affinity for many compounds. Therefore, PEBAX-2533 is considered as one of the best candidate materials for sorption of phenolic compounds [42].

2.4 Adsorption Isotherm Models

2.4.1 Langmuir Isotherm Model

In 1918, Langmuir used kinetic theory to derive an equilibrium model for monolayer adsorption, which is widely used to describe physical adsorption or chemisorption [46]. Based on Langmuir theory, the adsorption sites, which can hold adsorbed molecules, exist on the surface of the sorbents,

and the adsorbed molecules can be only fit on the specific sites, instead of the whole surface area. Hence, the adsorption process is also called specific adsorption, and it can be expressed as:



where A_1 is the free adsorbate molecule in solution, B_1 is the vacant sorption sites on the sorbent, and A_1B_1 represents the occupied sorption sites. k_a and k_d are the rate constant of adsorption and desorption, respectively. The Langmuir model is based on three main assumptions:

- i) The whole surfaces sites are alike without uneven structural features (e.g., dislocations).
- ii) There are no interactions between adsorbed molecules.
- iii) Only monolayers of molecules present on the adsorbent surfaces.

With the above assumptions, the adsorption and desorption rates can be written as:

$$rate_{ads} = k_a (N - N_j) C_e \quad (2)$$

$$rate_{des} = k_d N_j \quad (3)$$

where C_e , N , and N_j represent sorption equilibrium solution concentration, number of total potential sites, and number of occupied sites, respectively. $rate_{ads}$ decreases with the number of unoccupied adsorption sites $N - N_j$ decreasing; $rate_{des}$ increases with the number of occupied sites N_j . At equilibrium ($rate_{des} = rate_{ads}$), the equilibrium constant (K_L) is obtained as:

$$K_L = \frac{k_a}{k_d} = \frac{N_j}{(N - N_j) C_e} \quad (4)$$

Consequently, the fraction (θ) of adsorption sites occupied with molecules is defined as:

$$\theta = \frac{Q_e}{Q_m} = \frac{N_j}{N} = \frac{N - N_j}{N} K_L C_e \quad (5)$$

By rearranging the above equations, the Langmuir adsorption isotherm equation is expressed as:

$$\frac{Q_e}{Q_m} = \frac{C_e}{1 + K_L C_e} \quad (6)$$

which can be arranged as:

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L C_e} + \frac{1}{Q_m} \quad (7)$$

where Q_e represents the equilibrium adsorption capacity, Q_m represents the theoretical maximum adsorption capacity, K_L represents the Langmuir constant. **Equation 7** is the linearized form of the Langmuir isotherm model. Hence, the constants of Q_m and K_L can be calculated according to the slope and intercept of the $1/Q_e$ vs. $1/C_e$ plot.

2.4.2 Freundlich Isotherm Model

The Freundlich isotherm model was developed by Freundlich in 1909, and it is an empirical equation based on a large variety of adsorption experiments [47]. This empirical model is widely used to describe heterogeneous systems, and can be expressed as:

$$Q_e = K_F C_e^{1/n} \quad (8)$$

The above equation can be rearranged as:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

where Q_e is the equilibrium adsorption capacity, C_e is the equilibrium concentration of solute, n represents the intensity of adsorption, $1/n$ represents the heterogeneity factor, and K_F is the Freundlich constant characteristic of a particular adsorption isotherm. In general, Freundlich exponent n is 1-10 for most favorable adsorption process, and stronger interaction between adsorbent and adsorbate tends to have a larger n . **Equation 9** is the linearized form of the Freundlich isotherm model. Hence, the constants of K_F and $\frac{1}{n}$ can be calculated according to the slope and intercept of the $\ln Q_e$ vs. $\ln C_e$ plot.

2.4.3 Linear Isotherm Model

The linear isotherm model is also called Henry's adsorption isotherm, and it is considered as a special case of Freundlich isotherm model, where the Freundlich exponent n equals 1, which means that adsorption energies from all sites are identical [48]. This model is defined by:

$$Q_e = K_H C_e \quad (10)$$

where K_H represents the Henry's adsorption constant.

The above equation is the simplest isotherm model, and it usually can be used to describe the adsorption data better for systems with lower solute concentrations.

2.5 Adsorption Kinetic Models

2.5.1 Pseudo-First Order Kinetics Model

The pseudo-first order reaction kinetics model was investigated by Lagergren in 1989, and it has been widely used in numerous systems to provide valuable insights into the sorption process [49]. This model assumes that the sorption rate is proportional to the sorption capacity available, and it can be expressed as:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (11)$$

where Q_t refers to the solute uptake at time t , Q_e refers to the solute uptake at equilibrium, and k_1 refers to the pseudo-first order rate constant. **Equation 11** can be integrated with initial condition $t = 0, Q_t = 0$, gives,

$$\ln(Q_e - Q_t) = -k_1 t + \ln Q_e \quad (12)$$

The above equation is the linearized form of the pseudo-first order kinetics model [50]. Hence, the parameters of k_1 and Q_e can be calculated according to the slope and intercept of the $\ln(Q_e - Q_t)$ vs. t plot. In addition, **Equation 11** provides that the solute uptake rate is only based on the value of $Q_e - Q_t$, not on the solute concentration in the solution [51].

2.5.2 Pseudo-Second Order Kinetics Model

The pseudo-second order kinetics model was investigated by Ho and Mackay in 1990s with a focus originally on the sorption of batch metal onto peat. They found that chemical sorption with sharing or/and exchanging electrons between peat and batch metal ions occurred into the solution system [52]. This model can be expressed as:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (13)$$

where Q_t refers to the solute uptake at time t , Q_e refers to the solute uptake at equilibrium, and k_2 refers to the pseudo-second order rate constant. **Equation 13** can be integrated with initial condition $t = 0, Q_t = 0$, gives,

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (14)$$

The above equation is the linearized form of the pseudo-second order kinetics model. Similar to the pseudo-first order kinetic model, the parameters of k_2 and Q_e can be calculated according to the slope and intercept of the $\frac{t}{Q_t}$ vs. t plot.

It is assumed that, the rate limiting step for the pseudo-second order kinetic model is chemical sorption involving molecular interactions between sorbent and sorbate materials [50,53]. The pseudo-second order kinetic model has certain properties in common with the pseudo-first order kinetic model. The second order model also states that the solute uptake rate is only determined by the sorption capacity of the sorbent materials available, not the solute concentration [51].

2.5.3 Intra-Particle Diffusion Kinetics Model

In 1962, the intra-particle diffusion model was investigated by Weber and Morris based on a study of sorptive removal of biologically resistant pollutants from wastewater [54]. It has been found that in numerous sorption experiments, the solute uptake rate was proportional to $t^{1/2}$ in the initial sorption stage ($Q_t/Q_e < 0.5$), giving a linearized form of the intra-particle diffusion model. This model can be expressed as:

$$Q_t = k_i \sqrt{t} + C \quad (15)$$

where k_i refers to the intraparticle mass transfer constant, and C refers to the intensity of the boundary layer effect. The parameters of k_i and C can be calculated according to the slope and intercept of the Q vs. \sqrt{t} plot.

Considering the Q_t vs. \sqrt{t} plots from the above model, the intra-particle diffusion can be expected into three categories [55]:

- i) When Q_t vs. \sqrt{t} plot is linear, the intra-particle diffusion is a dominant factor in the sorption rate controlling steps.
- ii) When Q_t vs. \sqrt{t} plot is linear and the parameter C equals 0, the solute uptake rate is only determined by the intra-particle diffusion.
- iii) When Q_t vs. \sqrt{t} plot is linear and the parameter C does not equal 0, both intra-particle diffusion and boundary layer effects are likely considered as the dominant factors in the sorption processes.

Chapter 3

Isotherm Study for Bromophenols Sorption in PEBA

3.1 Introduction

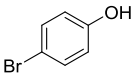
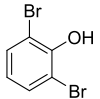
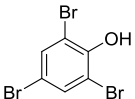
The study of sorption isotherm can be generally used to get an insight into the sorption type and mechanism. In this work, the sorption of BP, DBP, and TBP in PEBA was investigated under different conditions (i.e., temperature, and pH). The two commonly used isotherm models (Langmuir and Freundlich models) were used to fit the sorption data, and the sorption capacities of bromophenols on PEBA were estimated based on the fitted plots.

3.2 Experimental

3.2.1 Materials

PEBA 2533 SA01 (Arkema[®]), N,N - dimethylacetamide (anhydrous 99.8 %, Sigma-Aldrich[®]), 4-bromophenol (99%, Sigma-Aldrich[®]), 2,6-dibromophenol (97%, Sigma-Aldrich[®]), and 2,4,6-tribromophenol (99%, Sigma-Aldrich[®]) were obtained from commercial suppliers and used as received. Some chemical and physical properties of the sorbates (bromophenols) studied in this work are listed in **Table 1**.

Table 1 Chemical and physical properties of bromophenols studied in this work [56].

Molecular structure	Molar mass (g/mol)	Solubility in water (g/L at 293 K)	λ_{max} (nm)	pK _a
 4-bromophenol	173.01	14	279.5	9.17
 2,6-dibromophenol	251.90	0.90	308.0	6.67
 2,4,6-tribromophenol	330.80	0.061	312.5	5.97

3.2.2 Preparation of Polymeric Membrane Based Sorbent

A 15 wt.% PEBA 2533 solution in N, N - dimethylacetamide (DMAc) was made. The solution was heated in a water bath at 353 K with vigorous stirring for 3 hours. The homogenous mixture was allowed to sit at 343 K for 24 hours to avoid entrapped air bubbles. The solution was dispensed into preheated petri dishes by using volumetric glass syringes. The petri dishes were heated in an oven at 343 K for 24 hours to evaporate the organic solvent (DMAc). The formed PEBA membranes were washed several times with deionized water using ultrasonic cleaner (PM3-900TL, Prima[®], UK), and allowed to dry in a vacuum oven (VO400, Memmert[®], Germany) at 343 K for 8 hours to remove residual DMAc. The thickness and surface areas of the prepared PEBA sorbent were measured.

3.2.3 Determination of Sorption Equilibrium Uptake

This study involved batch sorption. In isotherm studies, the equilibrium uptakes Q_e for each bromophenol were determined by:

$$Q_e = \frac{V \times (C_0 - C_e)}{M} \quad (16)$$

where V is the volume of the solution (L) measured; M is the mass of PEBA sorbent (g); and C_0 and C_e represent the initial and equilibrium concentrations (mmol/L), respectively, which were measured using a UV-Vis spectrophotometer (UV-5500PC, Metash[®], China) at λ_{max} of each bromophenol. The calibration curves are presented in **Appendix B**. Prior to each run, all glasswares used were cleaned thoroughly.

3.2.4 Effects of Temperature

The batch adsorption of each bromophenol (BP, DBP, and TBP) on the PEBA membrane sorbent at different temperatures (298, 308, 318, and 328 K) was conducted as follows: 0.3 g of the PEBA membrane (thickness: $200 \pm 10 \mu\text{m}$) was placed into a 250-mL Erlenmeyer flask containing 150-mL aqueous solution of the bromophenol with different C_0 . For each bromophenol study, two flasks of solution with lowest and highest concentrations were left without PEBA membrane to serve as blanks.

Consequently, the capped Erlenmeyer flasks were sealed with parafilm and placed in a constant temperature shaker (SHA-B, Yamato Scientific[®], Japan) at a pre-set temperature. The above flasks were continuously shaken at 100 r/min for a period of 24 hours, to allow for equilibration of the

sorption process. In order to obtain data efficiently, four constant temperature shakers were running at the same time.

Finally, C_e of bromophenol at different temperatures were determined with the UV/Vis spectrophotometer at corresponding λ_{max} , and Q_e were calculated by **Equation 16**.

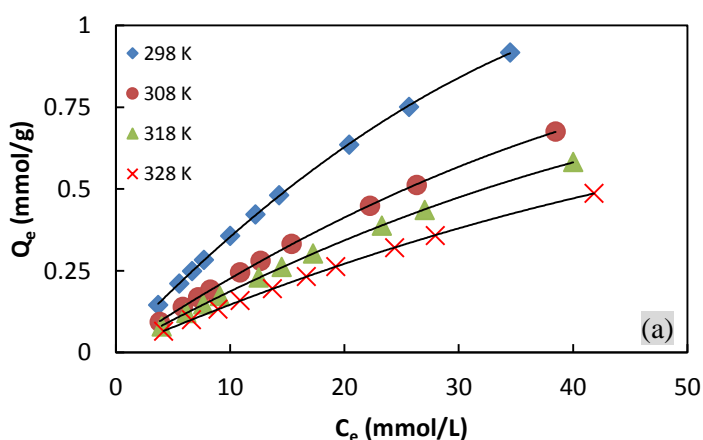
3.2.5 Effects of Solution pH

The adsorption of each bromophenol (BP, DBP, and TBP) on PEBA membrane at different initial pH was performed in a way similar to the procedure described in **Section 3.2.4**, except that, prior to adding the solution into the flasks, the initial pH (3, 5, 10, and 12) of stock solution for each bromophenol was adjusted by using HCl or NaOH. The pH of each solution sample was monitored by using a pH meter (SX-5150, Sanxin[®], China). In addition, all prepared samples were continuously shaken at room temperature (298 K), and equilibrium concentration C_e was determined using the UV/Vis spectrophotometer.

3.3 Results and Discussion

3.3.1 Effects of Temperature

The effects of temperature on the adsorption isotherms of BP, DBP, and TBP in PEBA membrane were examined in the range 298 – 323 K, and the results are shown in **Figure 5**.



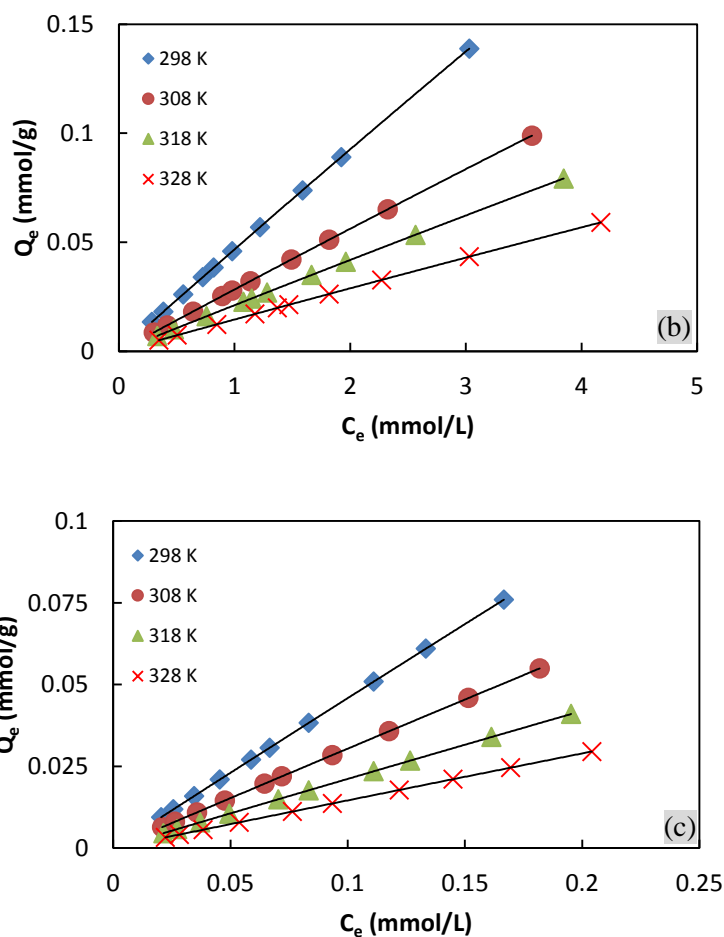


Figure 5 Sorption isotherms trend lines of (a) BP, (b) DBP, and (c) TBP in PEBA membrane at 298 – 323 K.

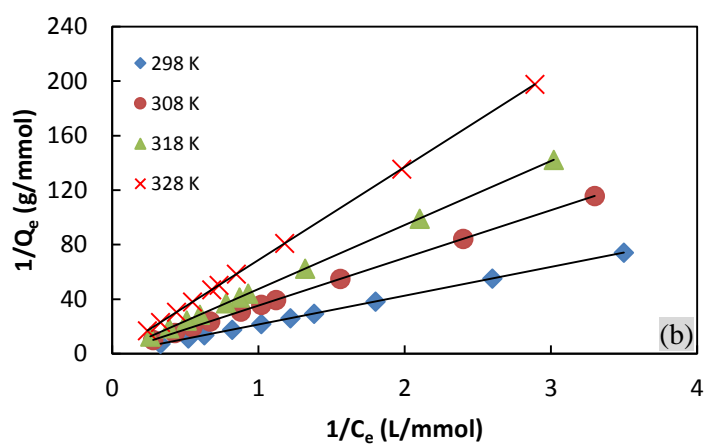
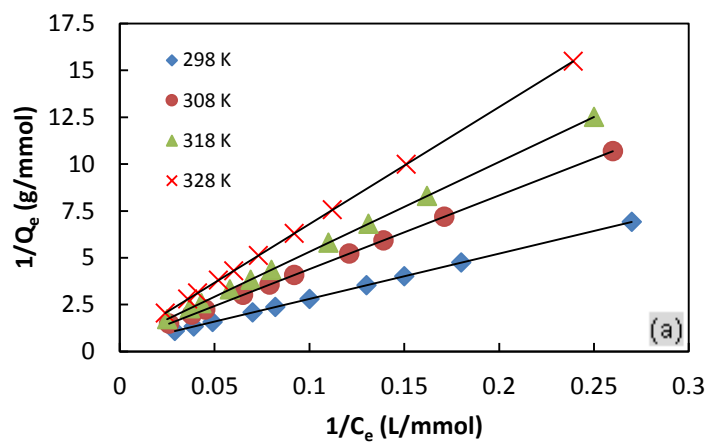
(membrane thickness = 200 μm , solution pH = 7)

Figure 4 shows that the sorption capacities of BP, DBP, and TBP in PEBA membrane were different. TBP had the highest sorption capacity, and PB had the lowest sorption capacity. Generally, the sorption of all three bromophenols was more pronounced at a lower temperature. As temperature increased, the equilibrium uptake of bromophenols on PEBA membrane decreased, which seems to suggest that the sorption of bromophenols in PEBA membrane was an exothermic process.

Then, the experimental data for BP, DBP, and TBP sorption onto PEBA membrane were fitted with two models, including:

- the linearized form of Langmuir isotherm model (**Equation 7**) by plotting $1/Q_e$ vs. $1/C_e$.
- the linearized form of Freundlich isotherm model (**Equation 9**) by plotting $\ln(Q_e)$ vs. $\ln(C_e)$.

They are shown in **Figures 6 - 7**. The model parameters and correlation coefficient (R^2) for both models are presented in **Table 2**.



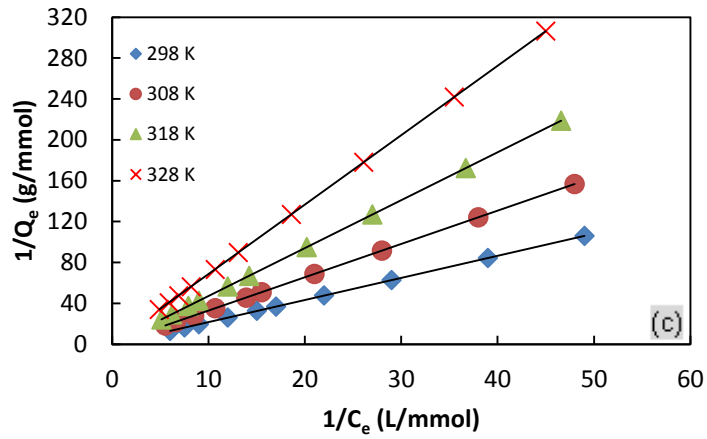
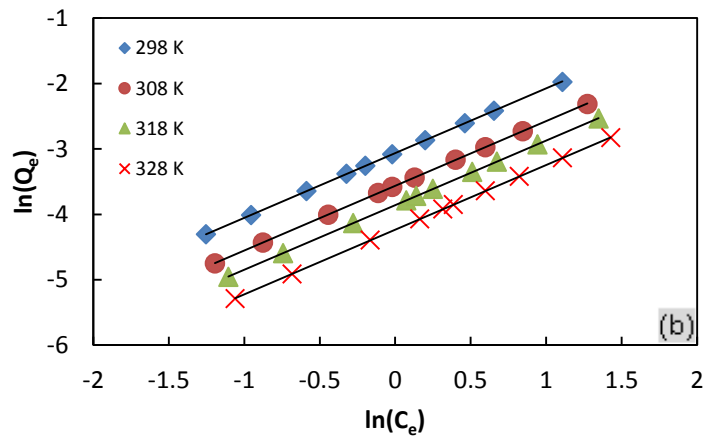
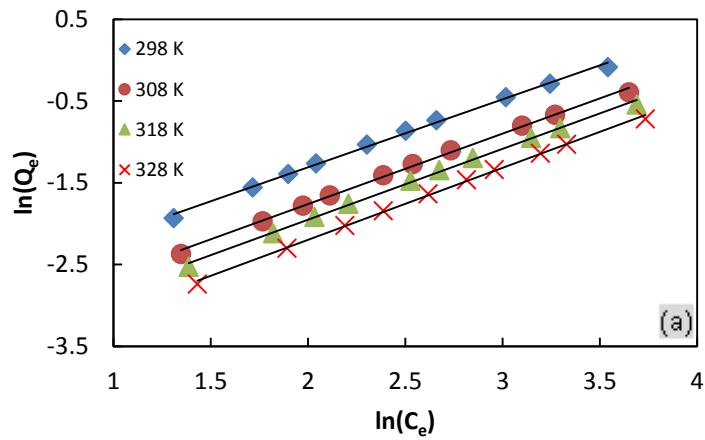


Figure 6 Langmuir isotherms fitted data for the sorption of (a) BP, (b) DBP, and (c) TBP on PEBA membrane at 298 – 323 K. (membrane thickness = 200 μm , solution pH = 7)



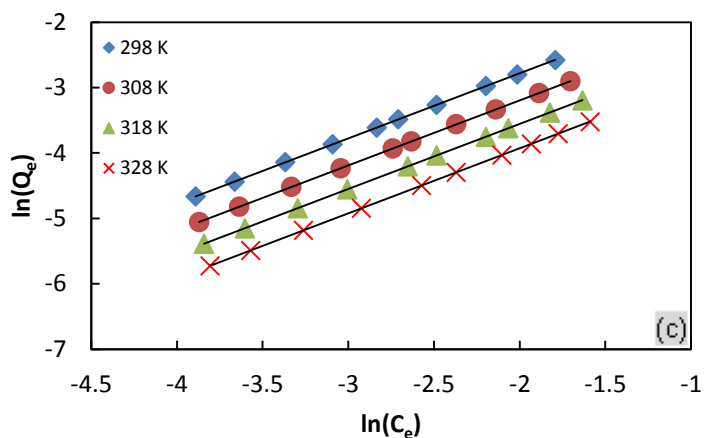


Figure 7 Freundlich isotherms fitted data for the sorption of (a) BP, (b)DBP, and (c) TBP on PEBA membrane at 298 – 323 K. (membrane thickness = 200 μm , solution pH = 7)

Table 2 Parameters of Langmuir and Freundlich isotherm models for sorption of BP, DBP, and TBP in PEBA membrane at different temperatures.

Bromophenols	Temperature (K)	Langmuir			Freundlich		
		Q_m (mmol/g)	K_L (L/mmol)	R^2	K_F (dimensions based on n)	$1/n$	R^2
BP	298	2.57	0.0161	0.998	0.0469	0.847	0.998
	308	2.19	0.0116	0.999	0.0257	0.867	0.997
	318	1.93	0.0108	0.997	0.0202	0.821	0.996
	328	1.83	0.0100	0.997	0.0177	0.825	0.997
DBP	298	4.55	0.0104	0.998	0.0473	0.988	0.997
	308	3.23	0.00886	0.997	0.0269	0.972	0.998
	318	2.44	0.00873	0.995	0.0214	1.02	0.997
	328	2.08	0.00897	0.996	0.0187	0.997	0.997
TBP	298	5.26	0.0879	0.995	0.549	1.03	0.995
	308	3.57	0.0859	0.997	0.315	1.01	0.998
	318	2.56	0.0832	0.998	0.219	0.996	0.998
	328	2.27	0.0818	0.997	0.202	1.02	0.998

As shown in **Figures 6 – 7**, for all three bromophenols, the experimental data were fitted well with both the Langmuir and Freundlich models at all temperatures, and the coefficient of determination (R^2) were high (>0.995). The results were in agreement with other studies. Bhatnagar [24] studied the removal of BP by industrial wastes, and it was found that the sorption isotherm of bromophenols could be expressed by the Langmuir and Freundlich equations. Anbia et al. [57] reported the sorption isotherm of BP on functionalized magnetic MCM-48 nanoporous silica by cyanuric chloride followed both models at various temperatures.

Since the sorption data were found to conform both the Langmuir and Freundlich equations, the performance of removing different bromophenols by PEBA membrane could be represented and compared by the values of Q_m and K_F . As shown in **Table 2**, an increase in temperature decreased the values of Q_m and K_F for BP, DBP, and TBP, which suggested that the sorption of all three bromophenols onto PEBA membrane was exothermic process. However, the value of $1/n$ remained almost constant, and it was not significantly affected by temperature.

Based on the Langmuir model parameters in **Table 2**, the maximum sorption capacities of PEBA membrane for BP, DBP, and TBP were found to be 2.57 mmol/g (at 298 K), 4.55 mmol/g (at 298 K), and 5.26 mmol/g (at 298 K), respectively. It was also seen from **Table 2** that the order of sorption in terms of Q_m or K_F on PEBA membrane is BP<DBP<TBP.

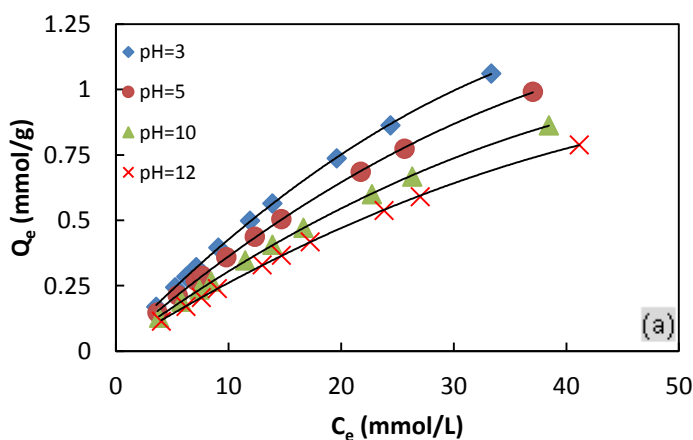
The type of bromophenols as characterized by their physical and chemical properties could influence their sorption capacities in PEBA. The solubility of BP, DBP, and TBP was considered as an important factor affecting sorption capacity. Normally, the sorption capacity of PEBA membrane was less for bromophenols with a high solubility than for phenols with a small solubility at same temperature. Specifically, the more soluble the bromophenol is, the less strongly would it tend to be adsorbed [58], which made the bromophenol molecule to be favored in the liquid phase. Of the three bromophenols studied here, the solubility of BP in water (14 g/L, 298 K) was the largest, resulting in the smallest sorption capacity in PEBA membrane, as seen from **Table 2**. Conversely, the solubility of TBP in water was the smallest, and the sorption capacity of TBP in PEBA membrane was observed to be the largest. This appeared to be due to the strong affinity between the hydrophobic PEBA membrane and the hydrophobic TBP molecules. This observation was in agreement with the results of Bhatnagar's study, which mentioned that an increase in solubility of the bromophenol was associated with a decrease in adsorption capacity [24].

Considering the chemical aspects of the solutes, molecules with electron withdrawing groups (e.g., -Br) were expected to affect adsorption to a great extent. Generally, it was observed that

stronger electron withdrawing groups are associated with an increase in adsorption capacity. Anbia et al. [57] compared the adsorption properties of BP and 4-chlorophenol (CP) on modified MCM-48 silica based adsorbent, and found the sorption capacity of CP was higher than that of BP, which appeared to be attribute the difference of electron withdrawing strength (-Cl was stronger than -Br). In addition, for the same functional groups with election withdrawing properties, more substitution on the phenolic molecules is related with an increase in adsorption capacity. For instance, the number of substituted electron withdrawing group (-Br) increased in the order BP<DBP<TBP, and the sorption capacity of three bromophenols on PEBA membrane increased in the order BP<DBP<TBP. Present result was in agreement with Bhatnagar's study, which reported that the sorption capacity of the di-substituted bromophenol was higher than that of the mono-substituted bromophenol on industrial wastes made adsorbents under the same conditions [24]. In some other studies, the molecular size of adsorbate was shown to affect adsorption. Specifically, the sorption capacity of a sorbent was less for larger solute molecules than that for smaller ones under the same conditions [54]. However, this was not consistent with the results of this study, since BP with the smallest size had the lowest sorption capacity among all three bromophenols studied here.

3.3.2 Effects of Solution pH

The effects of solution pH on the equilibrium adsorption of the three bromophenols on PEBA membrane were determined at temperature 298 K. The sorption isotherms for BP, DBP, and TBP in PEBA were shown in **Figure 8**.



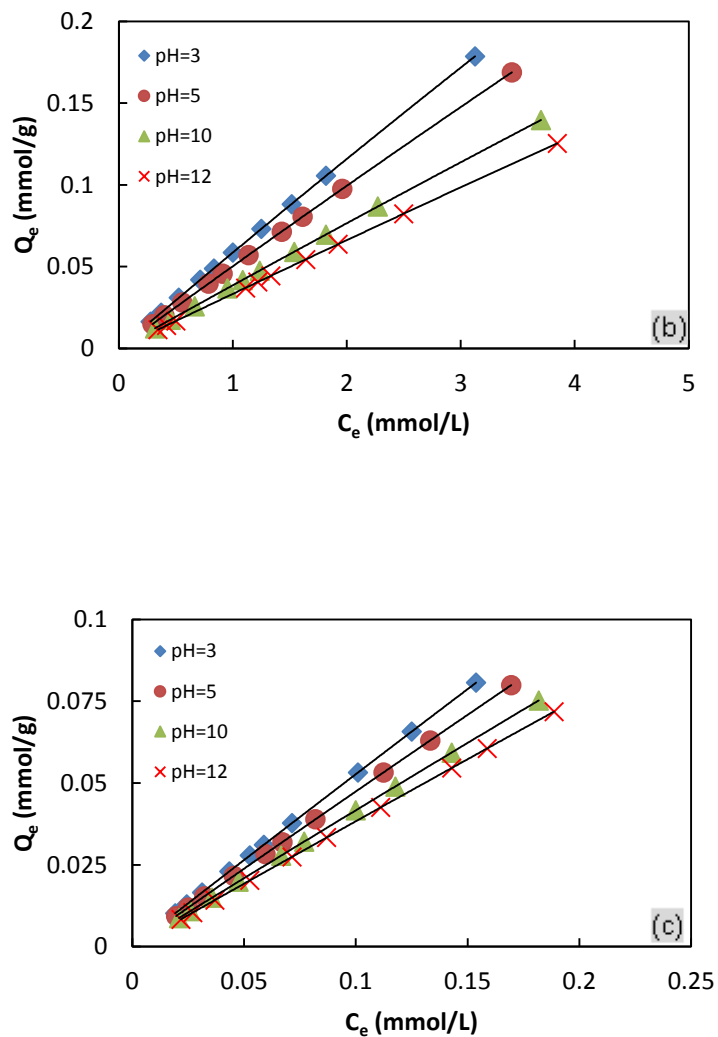


Figure 8 Sorption isotherms trend lines for the sorption of (a) BP, (b) DBP, and (c) TBP on PEBA under different pH at 298 K. (membrane thickness = 200 μm)

It is shown that as the solution pH increased, the sorption capacity of all three bromophenols on PEBA membrane decreased. **Figures 9 – 10** shows the data fitting to the linearized isotherm models, and the model parameters were determined and presented in **Table 3**.

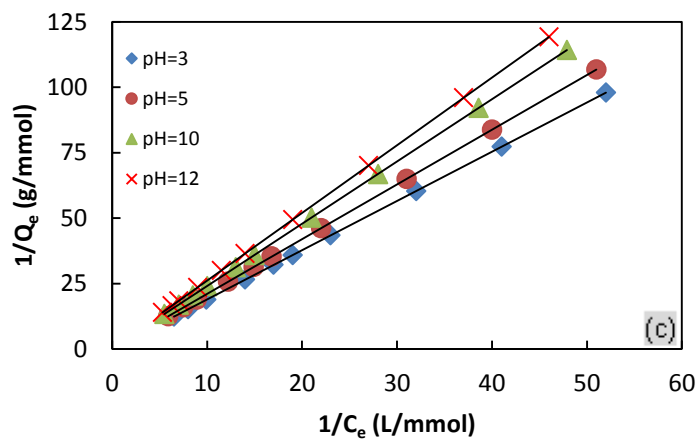
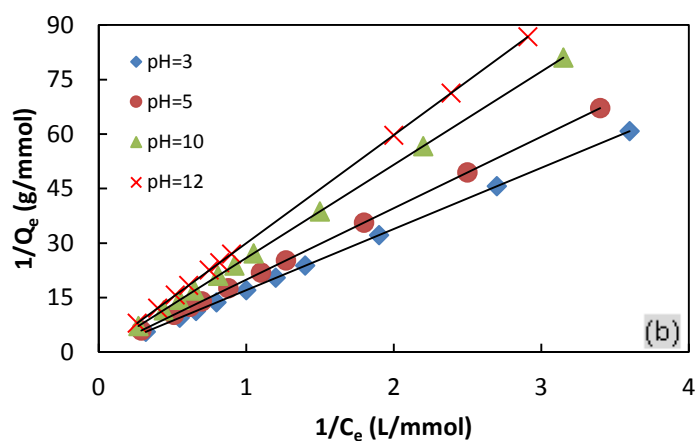
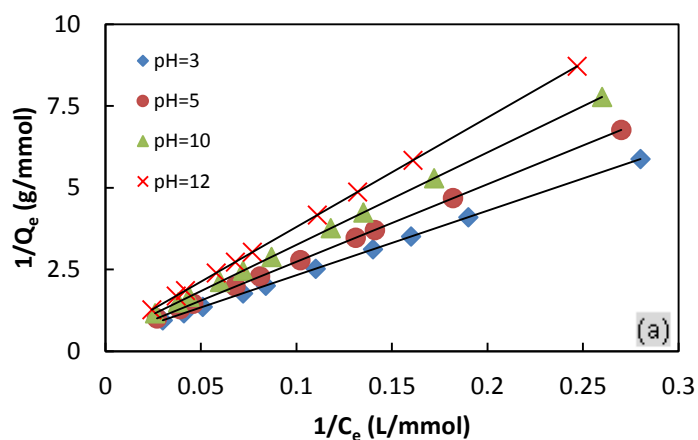


Figure 9 Langmuir isotherms fitted data for the sorption of (a) BP, (b) DBP, and (c) TBP on PEBA under different pH at 298 K. (membrane thickness = 200 μm)

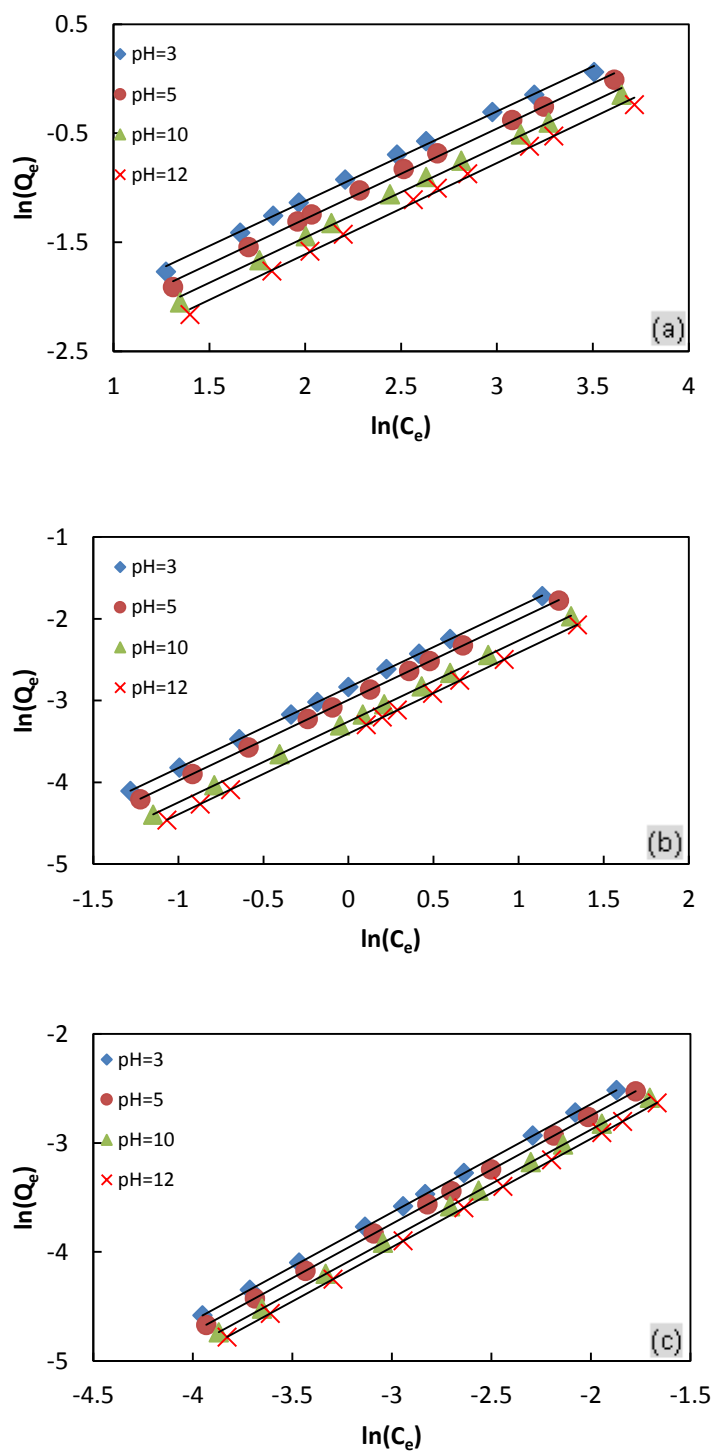


Figure 10 Freundlich isotherms fitted data for the sorption of (a) BP, (b) DBP, and (c) TBP on PEBA under different pH at 298 K. (membrane thickness = 200 μm)

Table 3 Parameters of Langmuir and Freundlich isotherm models for the sorption of BP, DBP, and TBP in PEBA membrane at different pH at 298 K.

Bromophenols	Initial pH	Langmuir			Freundlich		
		Q_m (mmol/g)	K_L (L/mmol)	R^2	K_F (dimensions based on n)	$1/n$	R^2
BP	3	2.86	0.0177	0.999	0.0628	0.823	0.999
	5	2.70	0.0156	0.999	0.0526	0.829	0.999
	10	2.37	0.0149	0.999	0.0442	0.832	0.999
	12	2.19	0.0136	0.999	0.0375	0.837	0.999
DBP	3	4.78	0.0124	0.999	0.0585	0.986	0.999
	5	4.62	0.0110	0.999	0.0502	0.987	0.999
	10	4.36	0.0089	0.999	0.0383	0.988	0.999
	12	4.09	0.0082	0.999	0.0333	0.989	0.999
TBP	3	5.66	0.0939	0.999	0.562	0.993	0.999
	5	5.38	0.0888	0.999	0.558	0.995	0.999
	10	5.02	0.0836	0.999	0.411	1.01	0.999
	12	4.90	0.0788	0.999	0.378	1.02	0.999

Figures 9 – 10 show that both the Langmuir and Freundlich models fitted the experimental data well. In addition, as shown in **Table 3**, the coefficient of determination (R^2) is high (>0.995), which indicated that it was reasonable to use either the Langmuir or Freundlich models to represent and compare the removal performance of PEBA membrane for all the three bromophenols studied.

Based on Langmuir model parameter Q_m , the data in **Table 3** show the sorption capacity at a given initial pH was in order of BP<DBP<TBP. As mentioned previously, the more soluble the bromophenol was, the less strongly it tended to be adsorbed on PEBA membrane.

On the other hand, as shown in **Table 3**, as the solution pH increased, the sorption capacity of an individual bromophenol on PEBA membrane decreased, and the sorption capacity was the highest (2.86 mmol/g for BP; 4.79 mmol/g for DBP; and 5.67 mmol/g for BP) at a pH of 3. It seemed that pH

can affect the solubility of the sorbent in the solution, resulting in a change in the sorption capacity. Since BP, DBP, and TBP were all weak acids ($pK_a < 4$), they are likely to be present as neutral species at a solution pH below their pK_a values. Conversely, the three bromophenols would be present as anionic species when the solution pH was above their pK_a values. In general, the solubilities of anionic species were higher than that of neutral species. Therefore, the bromophenols at a higher pH would be adsorbed less [59]. This observation was in agreement with the results of DiGiano, who reported that as the pH decreased, p-nitrophenol turned to be neutral molecules, which were adsorbed more easily onto carbon based adsorbent [60].

3.4 Conclusions

1. The equilibrium sorption of BP, DBP, and TBP in PEBA membrane obeyed both the Langmuir and Freundlich models.
2. The calculated model parameters showed that the sorption capacities of the bromophenols in PEBA increased in the order: BP < DBP < TBP. Bromophenols with low water solubilities had a larger sorption capacity in PEBA membrane than those with high water solubilities. Decreasing pH and increasing temperature increased the capacities of PEBA for bromophenol sorption.
3. The temperature dependence of the isotherm parameters suggested that the sorption of BP, DBP, and TBP onto PEBA was an exothermic process.

Chapter 4

Kinetics of Bromophenol Sorption in PEBA Membrane

4.1 Introduction

The study of sorption kinetics plays an important role in well-designed sorption process. In this study, the sorption kinetics was determined by measuring the solute uptake rate in order to obtain valuable information about the nature and mechanism of the sorption process.

4.2 Experimental

4.2.1 Effects of Sorbate Concentration

The adsorption kinetics studies were conducted at different adsorbate concentrations (BP: 30, 60, 90, 120, and 150 ppm; DBP: 30, 60, 90, 120, and 150 ppm; TBP: 20, 30, 40, 50, and 60 ppm) using 250-mL Erlenmeyer flasks with PEBA membrane samples of same thickness ($200 \pm 10 \mu\text{m}$); and mass (0.3 g). The flasks containing bromophenol solutions and PEBA sorbents were placed in a constant temperature shaker at a pre-set temperature (298 K). The UV/Vis spectrophotometer was used to measure the concentrations of the bromophenols at various intervals. Finally, the experimental data was analyzed based on 1st and 2nd order kinetics as well as intra-particle diffusion model.

4.2.2 Effects of Sorbent Forms, Thickness, and Size

To get an insight into the effects of sorbent on sorption performance, the batch adsorption kinetics studies were carried out at a constant initial concentration (60 ppm) and temperature (298 K) in 250 mL capped Erlenmeyer flasks.

PEBA sorbents with the same mass (0.3 g), but different forms (PEBA membrane with $200 \pm 10 \mu\text{m}$ in thickness; PEBA pellet with 1 mm in radius) were applied to evaluate the effects of sorbent forms in the sorption kinetics study.

PEBA membranes with the same surface area ($60 \pm 5 \text{ cm}^2$), but different thicknesses were used to evaluate the effects of sorbent thickness on the sorption kinetics.

PEBA pellets (radius: 1 mm) with the same mass (0.3 g) with and without cuts (non-cut, cut once, and cut twice) for each pellet were used to evaluate the effect of sorbent size in the sorption kinetics study.

Each sample was placed in the constant temperature shaker at a pre-set temperature and shaking speed. Finally, the concentrations of the bromophenols were determined throughout the sorption periods using the UV/Vis spectrophotometer.

4.2.3 Effects of Temperature

The adsorption kinetics at different temperatures was performed in the same way as described before, except that, the initial phenol concentrations were 60 ppm for three bromophenols, and the sorption experiments were performed at 298, 308, 318, and 328 K using a constant temperature shaker. Finally, the experimental data was analyzed to determine the activation energy involved in the sorption process.

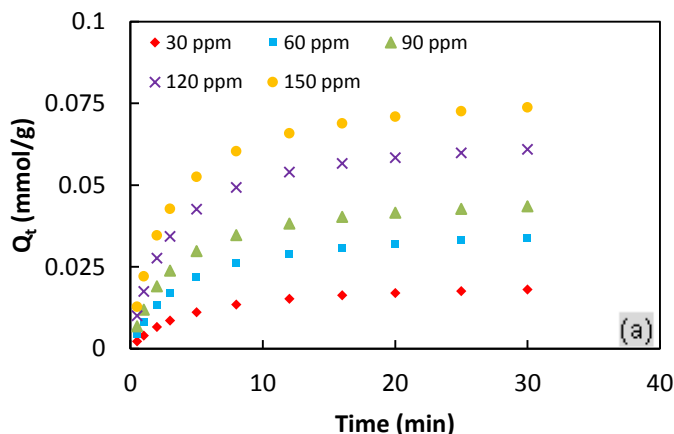
4.3 Results and Discussion

4.3.1 Effects of Sorbate Concentration

The sorption kinetics of BP, DBP, and TBP on PEBA membrane showed the evolution of the sorption capacity with time. In order to obtain the sorbate uptake at time t , **Equation 17** was used.

$$Q_t = \frac{V \times (C_0 - C_t)}{M} \quad (17)$$

where C_t refers to the solute concentration (mmol/L) of the bromophenol solution at time t (min). To analyze the kinetic data and find the best suitable model for the sorption process, pseudo-first order and pseudo-second order rate models were considered. The effects of initial phenol concentration on the sorption kinetics are shown in **Figure 11**.



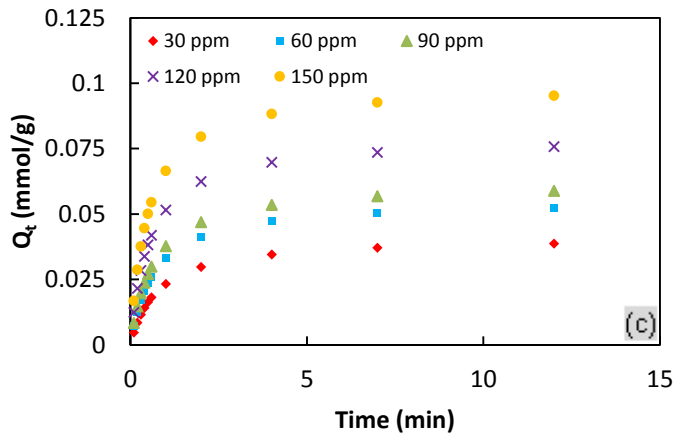
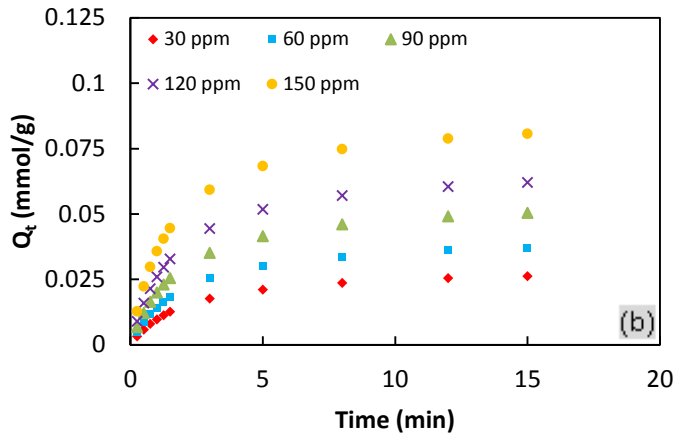


Figure 11 Kinetics of (a) BP, (b) DBP, and (c) TBP sorption by PEBA at different initial concentrations at 298 K.

The sorption kinetic data obtained at different initial feed concentrations of bromophenols were fitted to the pseudo-first (**Equation 12**) and pseudo-second (**Equation 14**) order rate models, as shown in **Figures 12 - 13**.

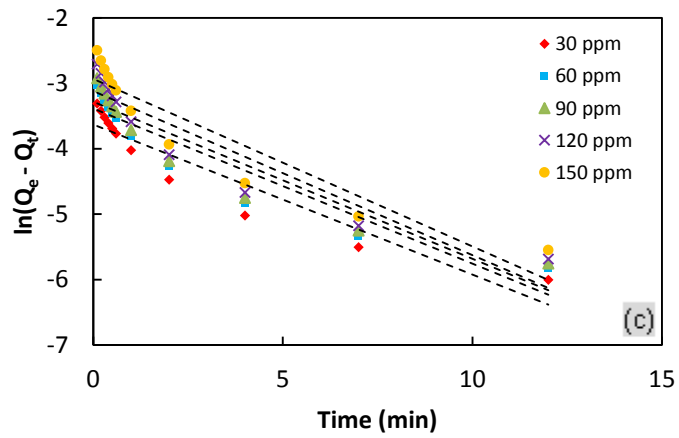
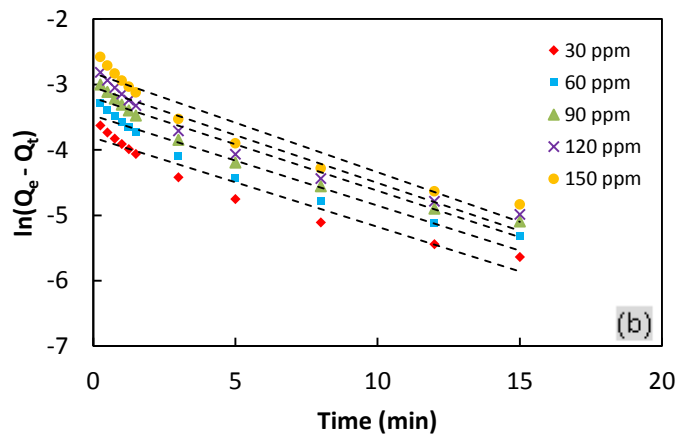
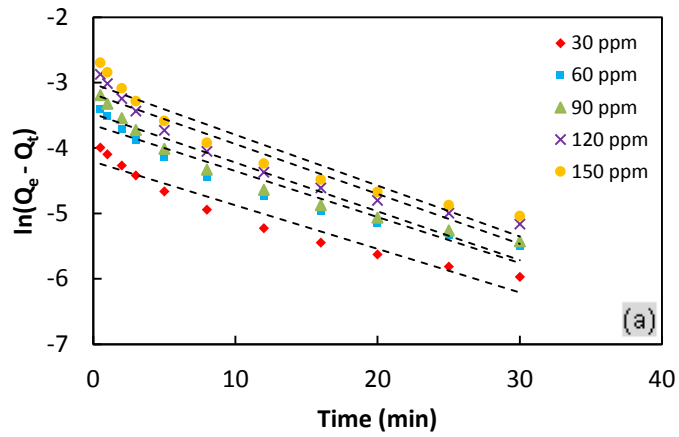


Figure 12 Linearized pseudo-first order model fitted data for TBP sorption on PEBA at different initial concentrations at 298 K.

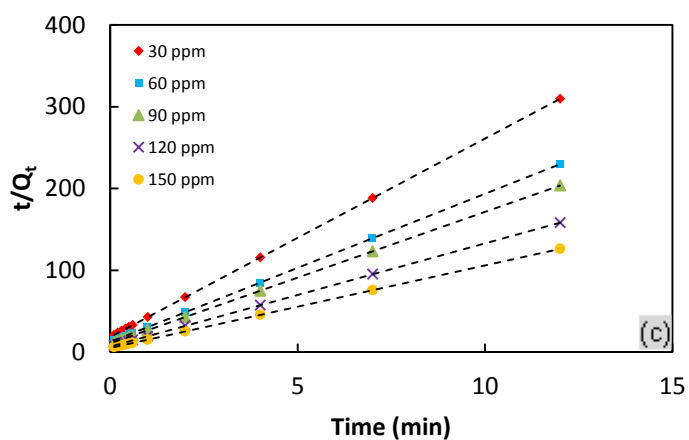
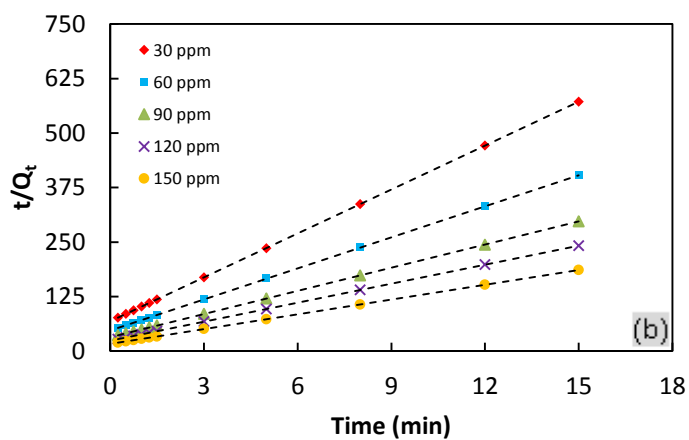
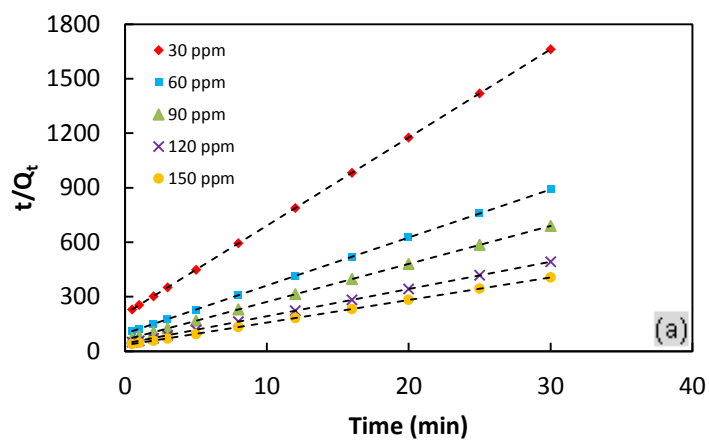


Figure 13 Linearized pseudo-second order model fitted data for TBP sorption on PEBA at different initial concentrations at 298 K.

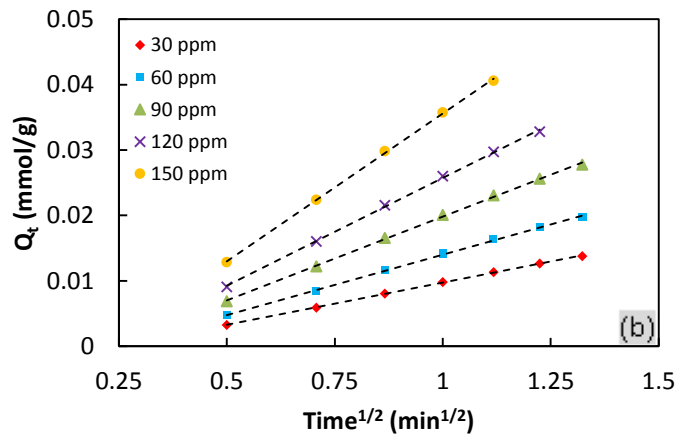
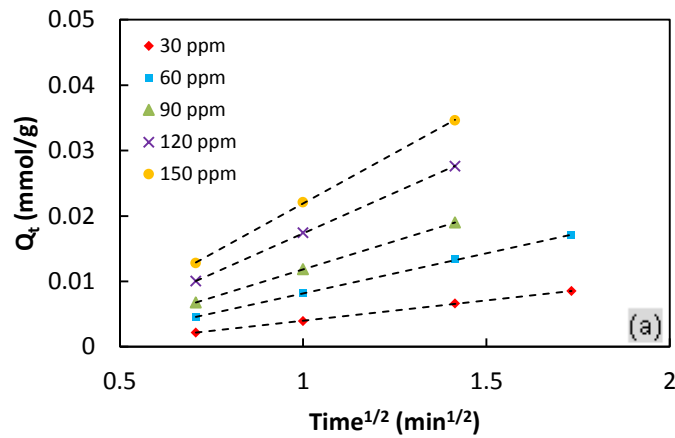
Table 4 summarized the sorption kinetic parameters based on the pseudo-first and pseudo-second order rate models calculated from the slopes and intercepts of the plots from **Figures 11 - 12**. The correlation coefficients (R^2) of the pseudo-second order mode fits were high (>0.995) for all three bromophenols, and the values of Q_e obtained from experiments remained similar to those predicted from the plots. The pseudo-second order rate model fitted the experimental data better than the pseudo-first order rate model. It was decided to use the pseudo-second order rate model to compare and explain the sorption of different bromophenols on PEBA membrane, although strictly speaking this model fitting is not without reservation [50,53]. Nevertheless, this analysis is simple to do for the purpose of comparing the sorption performance, and such a treatment is considered adequate here.

Table 4 Kinetic parameters of bromophenols sorption in PEBA membrane at different initial concentrations.

Bromophenols	Initial Conc. (ppm)	Pseudo-First Order			Pseudo-Second Order			Experimental Q_e (mmol/g)
		k_1 (min^{-1})	Q_e (mmol/g)	R^2	k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$)	Q_e (mmol/g)	R^2	
BP	30	0.0737	0.0181	0.928	11.4	0.0206	0.999	0.0201
	60	0.0747	0.0260	0.934	7.25	0.0378	0.999	0.0373
	90	0.0766	0.0327	0.922	6.87	0.0479	0.999	0.0473
	120	0.0769	0.0417	0.923	5.32	0.0666	0.998	0.0658
	150	0.0778	0.0490	0.920	4.73	0.0802	0.999	0.0798
DBP	30	0.0838	0.0265	0.907	16.4	0.0298	0.998	0.0289
	60	0.0839	0.0326	0.907	12.0	0.0421	0.999	0.0419
	90	0.0856	0.0392	0.904	9.72	0.0566	0.998	0.0558
	120	0.0875	0.0439	0.899	8.79	0.0689	0.998	0.0683
	150	0.0895	0.0511	0.894	7.63	0.0886	0.999	0.0882
TBP	20	0.0971	0.0282	0.867	31.8	0.0412	0.999	0.0399
	30	0.0986	0.0358	0.862	26.8	0.0552	0.998	0.0549
	40	0.0998	0.0423	0.864	25.0	0.0621	0.999	0.0618
	50	0.101	0.0544	0.869	23.6	0.0792	0.999	0.0788
	60	0.102	0.0687	0.875	20.5	0.0991	0.999	0.0989

4.3.2 Intra-Particle Diffusion Model

The intra-particle diffusion model was also used to fit the experimental data for the initial sorption stage ($Q_t/Q_e < 0.5$). The intra-particle diffusion model (**Equation 15**) fitting for sorption of the three bromophenols on PEBA at different initial phenol concentrations were shown in **Figure 14**, and the calculated model parameters were presented in **Table 5**.



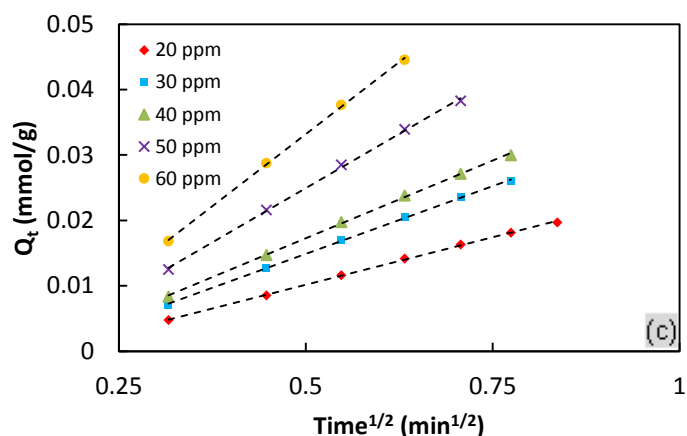


Figure 14 Intra-particle diffusion model fitted data for (a) BP, (b) DBP, and (c) TBP on PEBA.

Table 5 Parameters for intra-particle diffusion models of different initial concentrations of BP, DBP, and TBP on PEBA membrane.

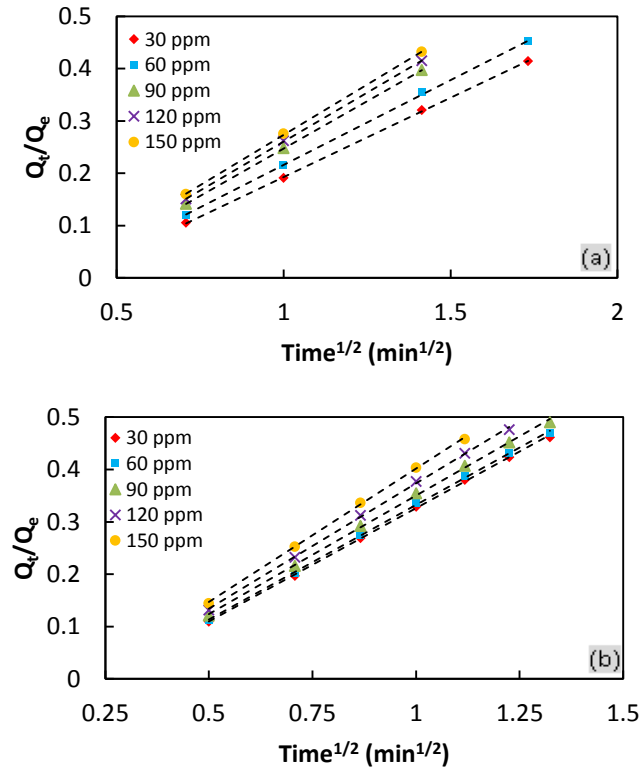
Bromophenols	Initial Conc. (ppm)	k_i (mmol g ⁻¹ min ^{-1/2})	C (mmol g ⁻¹)	R^2
BP	30	0.00620	-0.00232	0.998
	60	0.0123	-0.00413	0.998
	90	0.0173	-0.00552	0.999
	120	0.0249	-0.00756	0.999
	150	0.0308	-0.00892	0.999
DBP	30	0.0129	-0.00328	0.998
	60	0.0185	-0.00452	0.999
	90	0.0257	-0.00580	0.998
	120	0.0332	-0.00732	0.999
	150	0.0452	-0.00963	0.999
TBP	20	0.0292	-0.00433	0.998
	30	0.0415	-0.00592	0.998
	40	0.0475	-0.00651	0.999
	50	0.0664	-0.00826	0.995
	60	0.0882	-0.0108	0.999

As shown in **Figure 14**, the Q_t vs. $t^{1/2}$ plots were all linear but did not pass through the origin point, which indicated that boundary layer effects were not absent in the sorption process for the three bromophenols [61]. As can be seen from **Table 5**, as the initial phenol concentration increased, the values of parameter C also increased, which suggested that the boundary layer effect was more pronounced in the system. However, in view of the small C values, the boundary layer effect is certainly not significant.

In order to evaluate the effects of diffusion quantitatively, the slope of the fractional uptake (Q_t/Q_e) vs. $t^{1/2}$ plot (**Figure 15**) was used to estimate the intra-particle diffusivities (D_c , m^2/min) based on **Equation 18**:

$$\frac{Q_t}{Q_e} \approx \frac{4}{l} \left(\frac{D_c t}{\pi} \right)^{\frac{1}{2}} \quad (18)$$

where l represents the thickness (m) of the PEBA membrane. Similar to **Equation 15**, the above equation also works in the initial sorption stage ($Q_t/Q_e < 0.5$), where the sorption time is relatively short [62]. The results of diffusivities as evaluated are shown in **Table 6**.



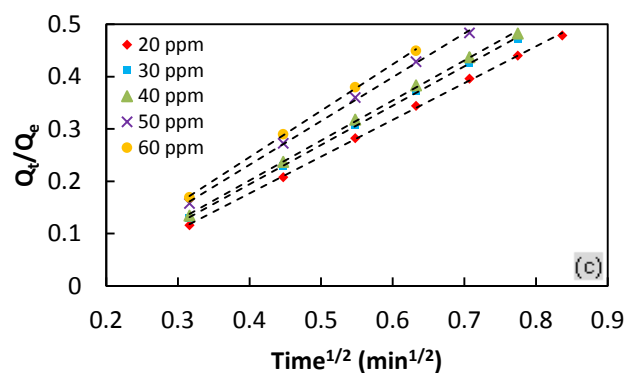


Figure 15 Fitted data for fractional sorption uptake of (a) BP, (b) DBP, and (c) TBP on PEBA membrane versus $t^{1/2}$.

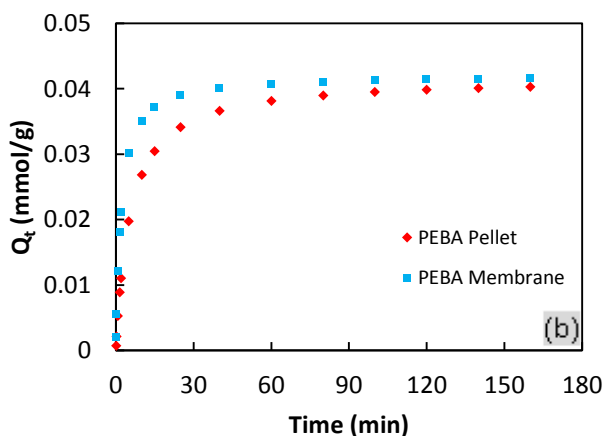
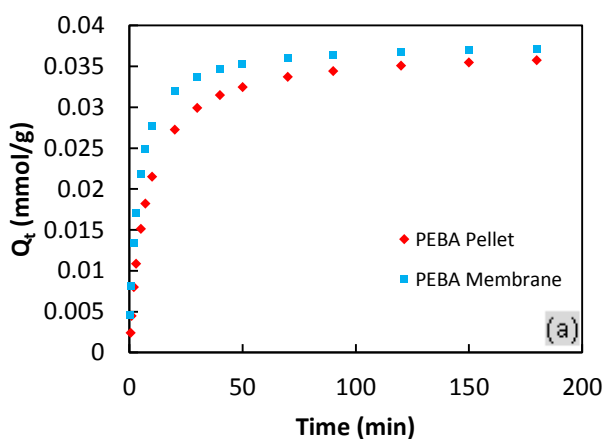
Table 6 Intra-particle diffusivity of different initial concentrations of BP, DBP, and TBP on PEBA membrane.

Bromophenols	Initial Conc. (ppm)	$D_c \times 10^{10}$ ($\text{m}^2 \text{min}^{-1}$)	R^2
BP	30	0.721	0.998
	60	1.07	0.999
	90	1.08	0.999
	120	1.09	0.999
	150	1.16	0.999
DBP	30	1.51	0.998
	60	2.26	0.999
	90	2.61	0.998
	120	2.80	0.999
	150	2.94	0.999
TBP	20	2.89	0.998
	30	2.93	0.998
	40	3.02	0.999
	50	3.11	0.099
	60	3.39	0.999

The data in **Table 6** show that the diffusivity of phenol in PEBA increased with an increased in the initial concentration of adsorbates (BP, DBP, and TBP). It appeared that, as the initial concentration of adsorbates increased, the sorption uptake of PEBA based sorbent also increased, leading the PEBA membrane to swell, making it easier for the solute molecules to diffuse in the membrane.

4.3.3 Effects of Sorbent Forms

To evaluate the advantages of using PEBA membranes over PEBA pellets for removing bromophenols, this section focused on the intra-particle diffusion study further. The sorption kinetics using the two forms of the sorbent (e.g., PEBA membrane vs. PEBA pellet) with same masses for sorption of BP, DBP, and TBP at same conditions is shown in **Figure 16**.



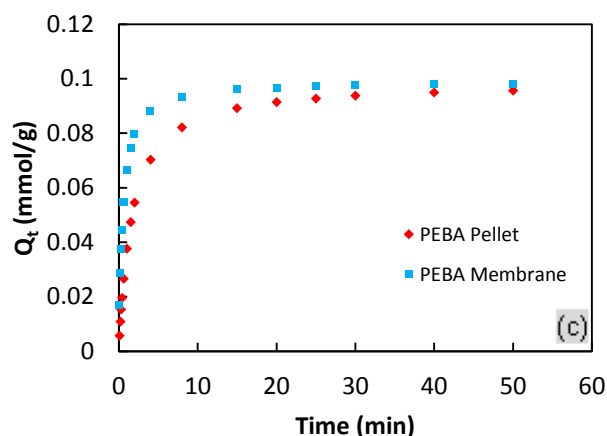
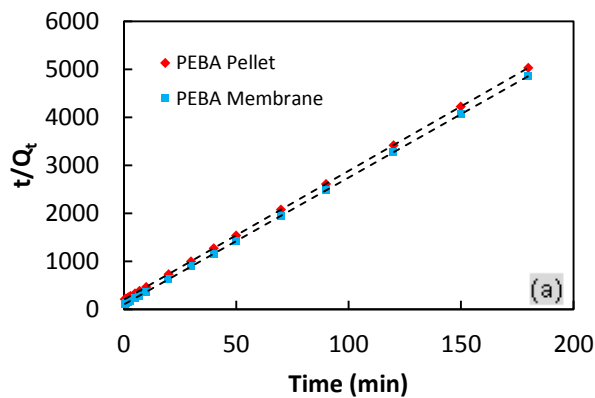


Figure 16 Kinetics of (a) BP, (b) DBP, and (c) TBP sorption by PEBA membrane vs. PEBA pellet.

(initial concentration = 60 ppm, temperature = 298 K)

Figure 16 (a) shows that under the same conditions, the sorption of BP on PEBA membrane reached equilibrium earlier than that using PEBA pellet, while the equilibrium sorption capacities were same for both forms of sorbents. Similar observations can be made in **Figure 16 (b)** for DBP and **Figure 16 (c)** for TBP. Generally, for PEBA based sorbent with a given mass, the surface area of thin PEBA membrane was larger than that of PEBA pellet. Therefore, the above results revealed that sorption of bromophenols in PEBA sorbent was not a simple surface phenomenon (i.e., adsorption), and the actual solute uptake should be an internal sorption process inside the PEBA based material.

Based on **Section 4.2.1**, the pseudo-second order model fit the experimental data well in kinetics studies. Hence, the above kinetics were fitted and analyzed with the pseudo-second order model only. The model curves were plotted in **Figure 17**, and the values of the model parameter values are presented in **Table 7**.



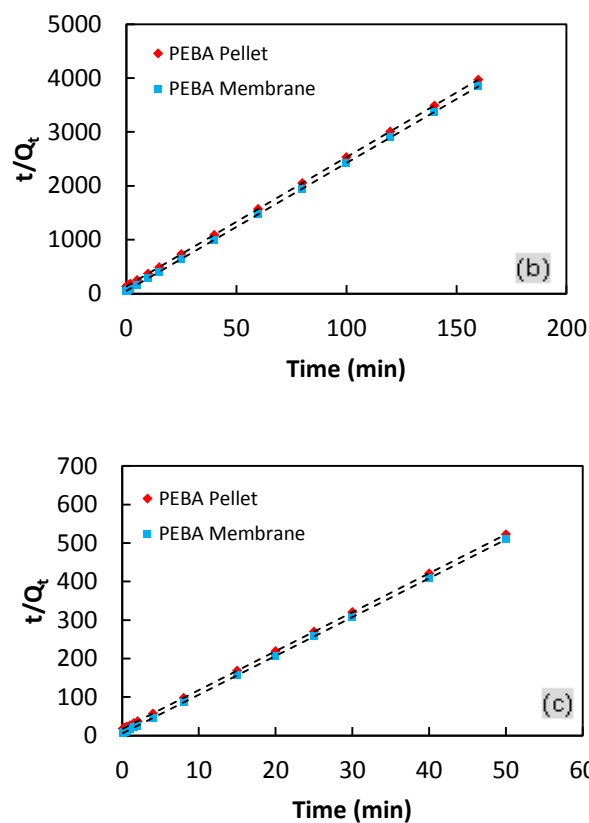


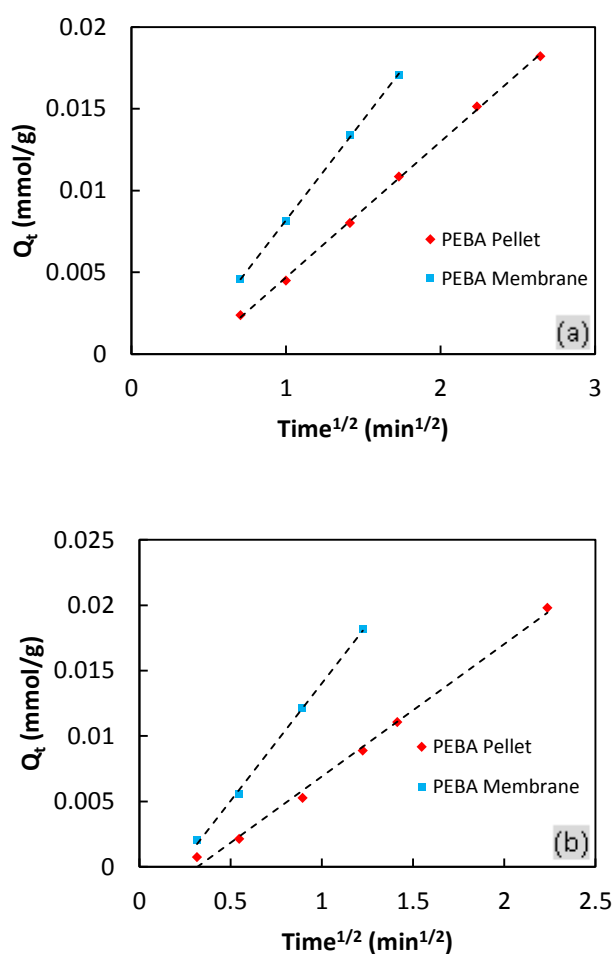
Figure 17 Linearized pseudo-second order model fitted data for (a) BP, (b) DBP, and (c) TBP sorption on PEBA membrane vs. pellet. (initial concentration = 60 ppm, temperature = 298 K)

Table 7 Pseudo-second order kinetic parameters of bromophenols sorption in PEBA membrane vs. PEBA pellet.

Bromophenols	Pellet (P) or Membrane (M)	k_2 (g mmol ⁻¹ min ⁻¹)	Q_e (mmol/g)	R^2	Experimental Q_e (mmol/g)
BP	P	3.68	0.0372	0.998	0.0370
	M	7.25	0.0378	0.999	0.0373
DBP	P	4.33	0.0417	0.998	0.0416
	M	12.0	0.0421	0.999	0.0419
TBP	P	6.22	0.0988	0.992	0.0986
	M	20.5	0.0991	0.999	0.0989

The data in **Table 7** shows the value of pseudo-second order rate constant (k_2) for PEBA membrane was larger than that for PEBA pellet for a given bromophenol. In other words, at the same conditions, as the surface area of PEBA increased, the value of k_2 increased. This observation was expected because a larger surface area of PEBA with a given mass means more liquid-PEBA interfacial contact. This revealed that the internal mass transfer mechanism inside the PEBA material should be also considered with the surface mechanism during the sorption process.

The intra-particle diffusion model (**Equation 15**) was also considered for phenol sorption on PEBA membrane and pellet, as shown in **Figure 18**.



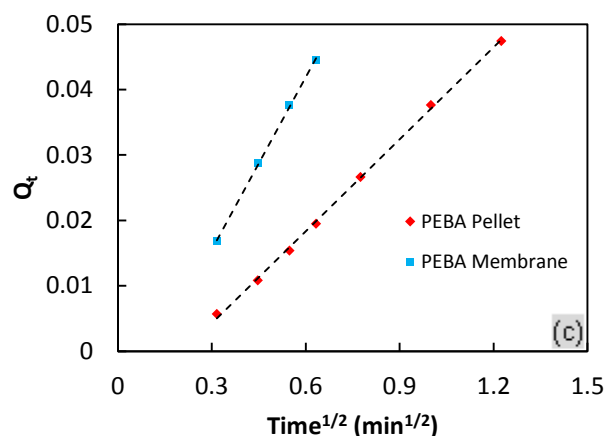


Figure 18 Intra-particle diffusion fitted data for sorption uptake of (a) BP, (b) DBP, and (c) TBP on PEBA membrane and pellet. (initial concentration = 60 ppm, temperature = 298 K)

Table 8 Parameters for intra-particle diffusion models of BP, DBP, and TBP in PEBA membrane and PEBA pellet.

Bromophenols	Pellet (P) or Membrane (M)	Intra-Particle Diffusion Parameters		
		k_i (mmol g ⁻¹ min ^{-1/2})	C (mmol g ⁻¹)	R^2
BP	P	0.00830	-0.00363	0.999
	M	0.0123	-0.00413	0.999
DBP	P	0.0101	-0.00322	0.998
	M	0.0185	-0.00452	0.999
TBP	P	0.0469	-0.00980	0.999
	M	0.0882	-0.0108	0.999

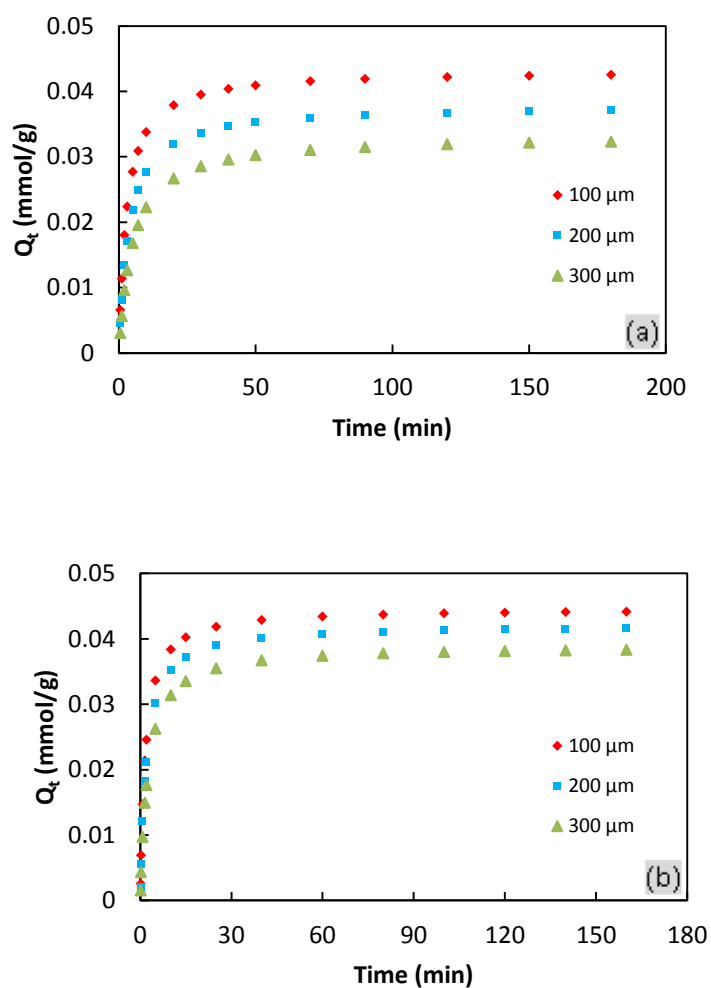
It was shown that the PEBA sorbent sizes (membrane thickness, pellet diameter) can affect the intra-particle diffusion of bromophenol. The above results seem to suggest that intra-particle diffusion is not the dominant mass transfer mechanism during the sorption process, which further supported the conclusion in **Section 4.3.2**.

Table 4 also showed that as PEBA material changed from pellet to film, resulted in an increase in value of D_c . D_c described the internal diffusion rate, which was not related to the thickness or surface area of the sorbent. The value of D_c was obtained from the slope of (Q_t/Q_e) vs. $t^{1/2}$ plot with

the assumption that internal diffusion was 100% contributed to the sorption process. Clearly, the intra-particle diffusion is not a reasonable dominating mechanism of phenol sorption in PEBA.

4.3.4 Effects of Sorbent Thickness

To study the effect of PEBA membrane thickness with a given surface area on sorption process, the sorption uptakes for the three bromophenols were examined over time. The sorption kinetics data of PEBA membrane with the same surface area but different thicknesses for BP, DBP, and TBP is shown in **Figure 19**.



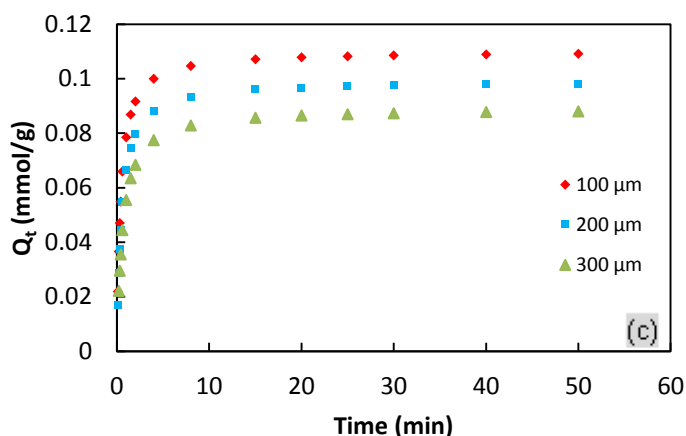


Figure 19 Uptake of (a) BP, (b) DBP, and (c) TBP on 60 cm² PEBA membrane with different thicknesses.

As shown in **Figure 19**, for the PEBA membrane with a given surface area, the sorption uptake of bromophenol decreased with an increase in the membrane thickness. Generally, the sorption capacity was proportional to the surface area of the sorbent for simple surface sorption if the sorption occurs only on the surface. Apparently, for the systems studied here, phenol sorption has occurred in the interior of PEBA sorbent.

4.3.5 Effects of Sorbent Size

Previous sections described sorptive removal of bromophenols from water by using PEBA membrane. However, due to the cost and procedure of producing membranes, pellet sorbents are still considered in industries. Usually, the commercial stock pellet was ground to smaller particles, which are expected to show better sorption capacity than original pellets. To compare the sorption properties of PEBA pellet of different sizes, and to further support that diffusion was not the only factor contributing to the mass transfer, the sorption uptakes of the three bromophenols in PEBA were examined over time. The sorption kinetics data of PEBA pellet with the same mass but different cutting sizes were shown in **Figure 20**.

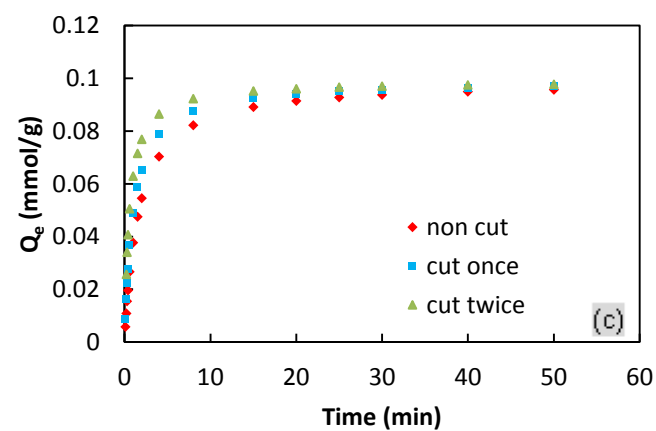
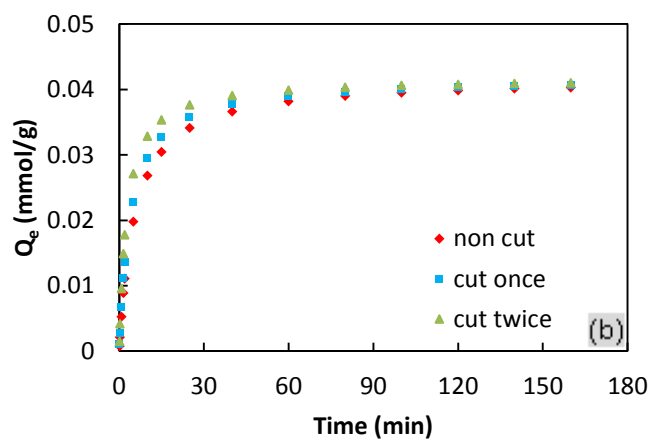
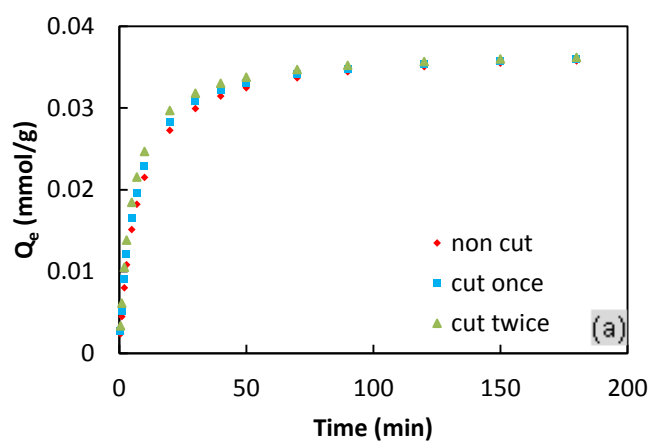
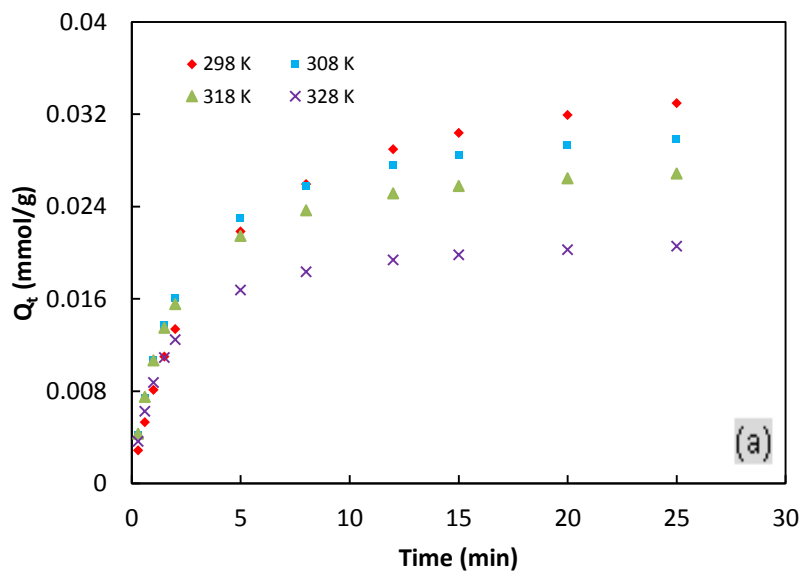


Figure 20 Uptake of (a) BP, (b) DBP, and (c) TBP on 0.3 g PEBA membrane with different cutting numbers.

As can be seen from **Figure 20**, the sorption capacities of PEBA pellets with different cuts were same. For PEBA pellets with a given mass, a decrease in size leads to a high surface area. Increased surface area did not change the equilibrium sorption capacity, suggesting again that the sorption process was not occurring by a simple surface phenomenon. This is in agreement with the previous results. Meanwhile, it was also shown that, instead of using PEBA membrane sorbent, using PEBA pellet sorbent with small sizes and high surface area was also feasible to remove bromophenols. However, the use of minute particles may result in significant presence drop for the liquid, which could be a significant operating issue. In addition, the PEBA pellet showed lower sorption performance than PEBA membrane, and its isolation was not as easy as film based sorbent.

4.3.6 Effects of Temperature

To investigate the effect of temperature on the sorption rate, the rates of sorption uptakes for the three bromophenols were examined at different temperatures. **Figure 21** shows the amount of phenols sorbed into PEBA.



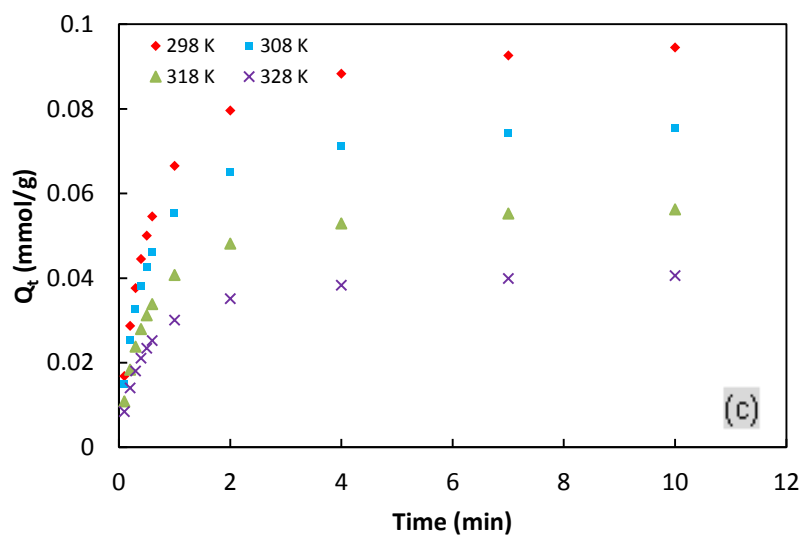
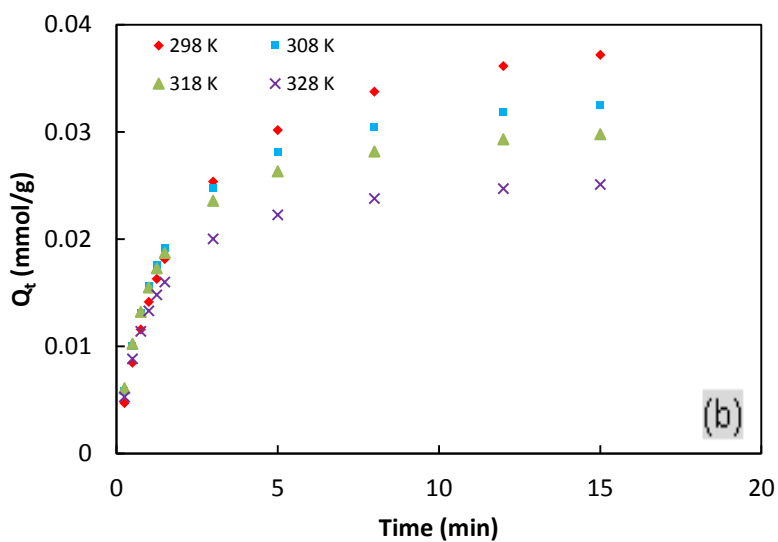


Figure 21 Kinetics of (a) BP, (b) DBP, and (c) TBP sorption on PEBA membrane at various temperatures. (initial concentration = 60 ppm, membrane thickness = 200 μm)

The pseudo-second order model was used to fit to the experimental data, as shown in **Figure 22**. The model parameters presented in **Table 9**.

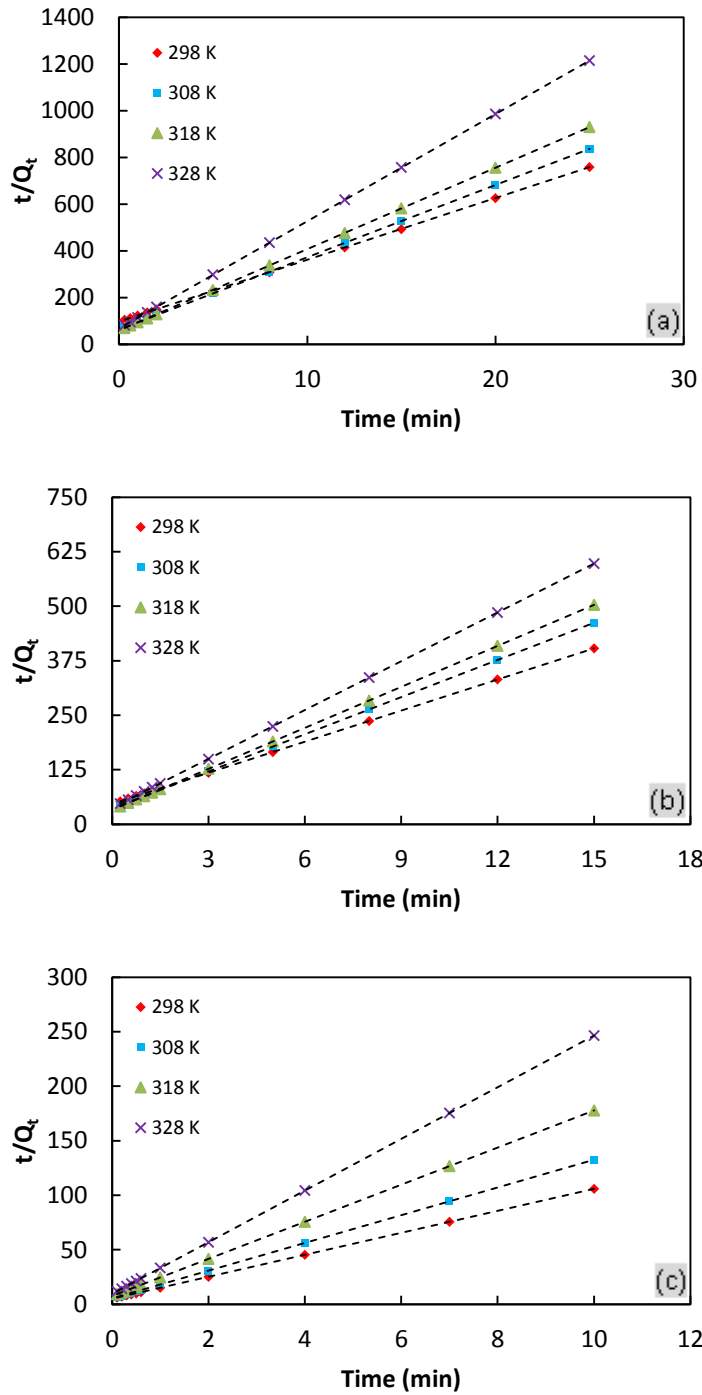


Figure 22 Linearized pseudo-second model fitted data for (a) BP, (b) DBP, and (c) TBP sorption on PEBA at various temperatures. (initial concentration = 60 ppm, membrane thickness = 200 μm)

Table 9 Kinetic parameters of bromophenols sorption in PEBA membrane at various temperatures.

Bromophenols	Temperature (T)	k_2 (g mmol ⁻¹ min ⁻¹)	Q_e (mmol/g)	R^2	Experimental Q_e (mmol/g)
BP	298	7.25	0.0378	0.999	0.0373
	308	15.2	0.0323	0.999	0.0320
	318	20.6	0.0287	0.099	0.0286
	328	30.9	0.0218	0.998	0.0215
DBP	298	12.0	0.0421	0.999	0.0419
	308	22.5	0.0352	0.999	0.0350
	318	29.6	0.0319	0.099	0.0315
	328	36.7	0.0268	0.999	0.0266
TBP	298	20.5	0.0991	0.999	0.989
	308	29.9	0.0787	0.998	0.783
	318	38.6	0.0587	0.099	0.585
	328	58.7	0.0422	0.999	0.421

As the data in **Table 9** shows, at a higher temperature, the uptake rate increased but the equilibrium uptake capacity decreased. Therefore, with a change in temperature, there is a pronounced trade-off between sorption capacity and sorption rate in the system.

4.3.7 Activation Energy

Activation energy (E_a , kJ/mol) describes the energy barrier that needs to overcome for sorption to happen in the system, and it can be written in an Arrhenius type:

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (19)$$

where k refers to sorption rate constant (L/mmol), A is a frequency factor, R (kJ/mol K) is the universal gas constant, and T is the temperature (K). To calculate the value of activation energy, **Equation 19** can be arranged to a linear form:

$$\ln k = \ln A - \frac{E_a}{R \cdot T} \quad (20)$$

where E_a and A can be calculated from the slope and intercept of the $\ln k$ vs. $1/T$ plot. The $\ln k$ vs. $1/T$ plots for the sorption of the three bromophenols in PEBA are depicted in **Figure 23**, and the calculated A and E_a values are listed in **Table 10**

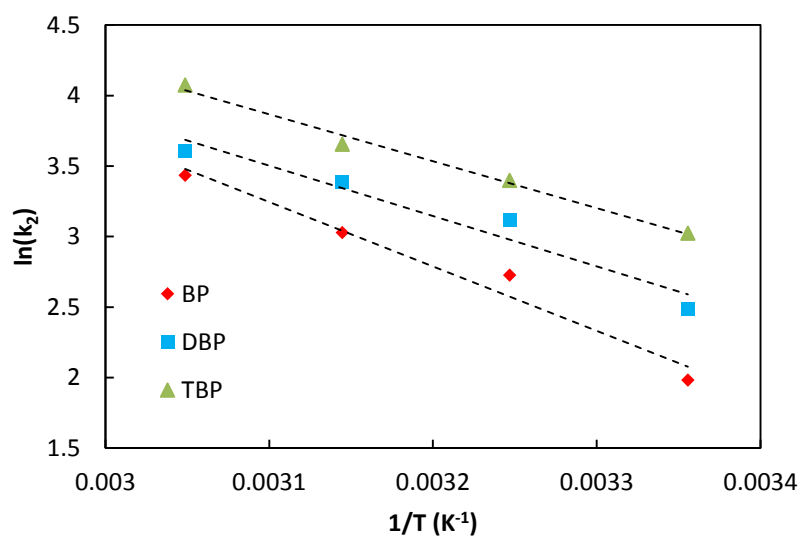


Figure 23 Linearized Arrhenius equation fitted data for BP, DBP and TBP sorption on PEBA membrane.

Table 10 Activation energy for sorption based on pseudo-second order rate constant of BP, DBP, and TBP in PEBA.

Bromophenols	E_a (kJ mol ⁻¹)	R^2
BP	38.0	0.969
DBP	29.6	0.945
TBP	27.6	0.990

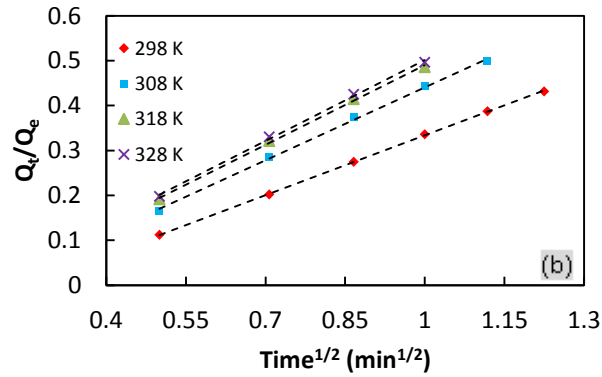
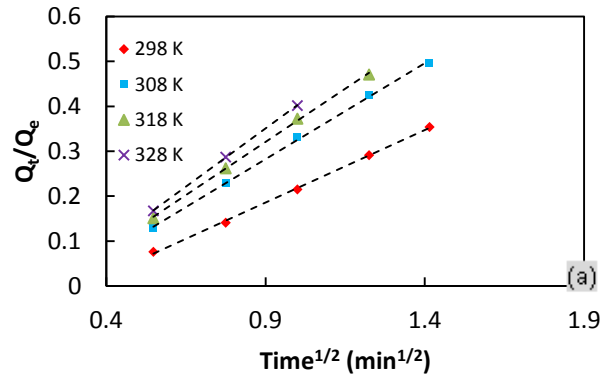
If diffusion mechanism were the primary controlling step in the sorption process, then the activation energy E_a (kJ/mol) could be described by:

$$D_c = D_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (21)$$

where D_0 refers to the temperature independent pre-exponential factor [63]. To calculate the value of activation energy based on the experimental data, **Equation 21** may be arranged to a linear form as following equation:

$$\ln D_c = \ln D_0 - \frac{E_a}{R \cdot T} \quad (22)$$

where the parameters of E_a and D_0 can be obtained from the slope and intercept of the $\ln D_c$ vs. $1/T$ plot. The value of D_c based on the experimental data from **Section 4.3.6** was calculated from the slope of (Q_t/Q_e) vs. $t^{1/2}$ plot, which was depicted in **Figure 24**, and the calculated D_c values are listed in **Table 11**.



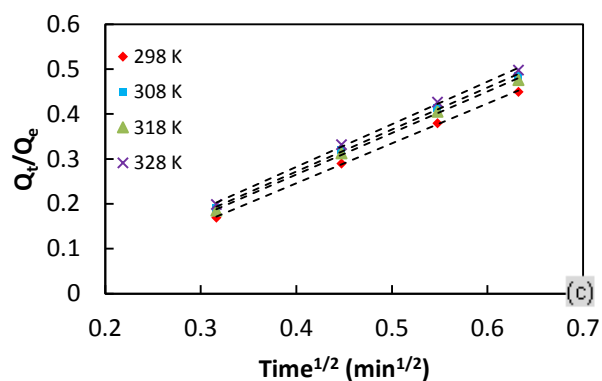


Figure 24 Fitted data for fractional sorption uptake of (a) BP, and (b) DBP, and (c) TBP on PEBA versus $t^{1/2}$ at various temperatures. (initial concentration = 60 ppm, membrane thickness = 200 μm)

Table 11 Intra-particle diffusivity of different initial concentrations of BP, DBP, and TBP on PEBA membrane at various temperatures.

Bromophenols	Temperature (K)	$D_c \times 10^{10}$ ($\text{m}^2 \text{min}^{-1}$)	R^2
BP	298	1.07	0.999
	308	2.15	0.999
	318	3.59	0.999
	328	5.00	0.999
DBP	298	2.26	0.999
	308	3.78	0.998
	318	5.47	0.998
	328	7.56	0.998
TBP	298	3.39	0.999
	308	5.41	0.999
	318	7.12	0.998
	328	9.96	0.998

Then the $\ln D_c$ vs. $1/T$ plots for the three bromophenols are depicted in **Figure 25**, and the calculated D_0 and E_a values are listed in **Table 12**.

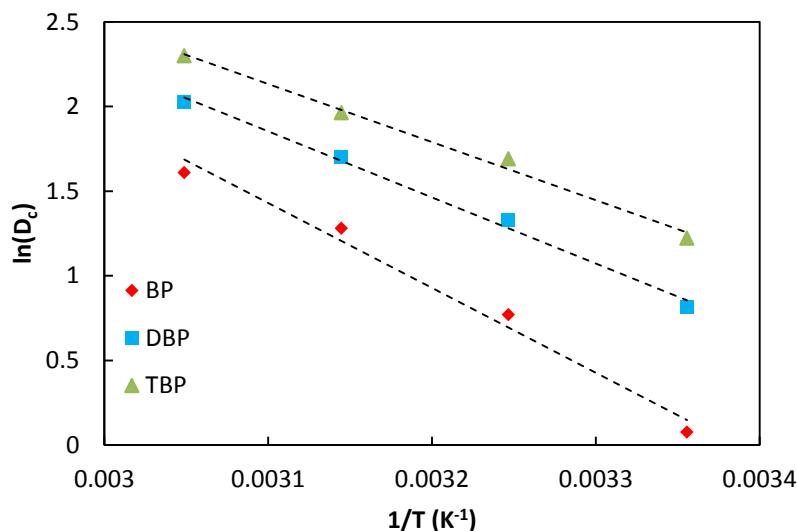


Figure 25 Linearized Arrhenius-type of equation (if dominated by diffusion) fitted data for BP, DBP, and TBP sorption on PEBA membrane.

Table 12 Activation energy for intra-particle diffusivity for sorption of BP, DBP, and TBP on PEBA membrane at various temperatures.

Bromophenols	E_a (kJ mol ⁻¹)	R^2
BP	41.7	0.983
DBP	32.4	0.993
TBP	28.5	0.991

It can be seen that for a given bromophenol, the value of activation energy obtained from **Equation 20** was similar to that obtained from **Equation 22**. Either model could be applied to the study of activation energy for sorption of the three bromophenols on PEBA membrane. Morris et al. [54] indicated that, if diffusion mechanism was the only factor dominating the mass transfer for adsorbents with large molecular sizes, then the activation energy was in the range of 12-21 kJ/mol. The

results revealed again that intra-particle diffusion was not the dominating mass transfer mechanism during the sorption process, which was in agreement with the conclusions drawn in **Section 4.3.2** and **4.3.3**.

4.4 Conclusions

1. The kinetics of BP, DBP, and TBP sorption in PEBA membrane obeyed the pseudo-second order kinetics model.
2. The sorption uptake occurred not only on surface, the phenol molecules also entered the interior of the PEBA sorbent.
3. The sorption kinetics results showed that the processing of PEBA pellets to PEBA membranes improved its sorption rate. A decrease in the membrane sorbent thickness increased both sorption rate and capacity, and the cutting of PEBA pellets to smaller sizes increased its sorption rate only. The kinetics data analysis also supported that diffusion was not the dominating mechanism in sorption.
4. The rate constant based on the pseudo-second order kinetics model and diffusivity coefficient based on the intra-particle diffusion model were both temperature dependent, and the temperature dependencies followed Arrhenius type of relations.

Chapter 5

Use of PEBA Sorbent to Treat Waste Effluent from Tetrabromobisphenol A Industry

5.1 Introduction

Tetrabromobisphenol A (TBBPA), which belongs to both bisphenol A (BPA) and bromophenol categories [64], is a toxic white powder at room temperature [65,66]. Its solubility in water is 0.063 mg/L at room temperature [70], and its structure is shown in **Figure 26**. As mentioned in earlier sections, there are wide practical applications for bromophenol in industries. For instance, TBBPA can be used as an intermediate to produce epoxy, polyester, ABS, HIPS, plastics, or coating material for facilitating the fire retardant property [67,68].

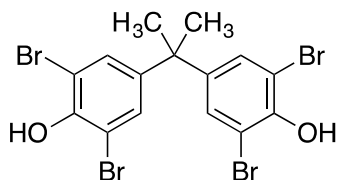


Figure 26 Molecular structure of TBBPA.

TBBPA is primarily synthesized by bromination of BPA, as shown in **Figure 27**. Depending on reaction conditions, three methods have been used to prepare TBBPA, including direct bromination, catalytic bromination, and oxidation-bromination [69].

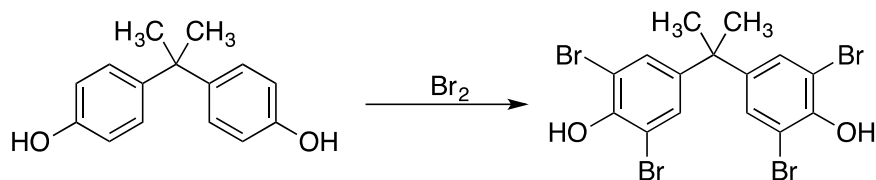


Figure 27 Synthesis of TBBPA with BPA.

Exploitation of halogen resources, such as bromine and bromine derivatives, has been an important part of ocean economy. Shandong Tianyi Chemical Co., Ltd. (TY), a core operating company of Shandong Research Institute of Ocean Chemical Industry (Weifang, China), has been a major

TBBPA supplier with a production capacity of (1,5000 mt/year). The production route for TBBPA can be illustrated as follows:

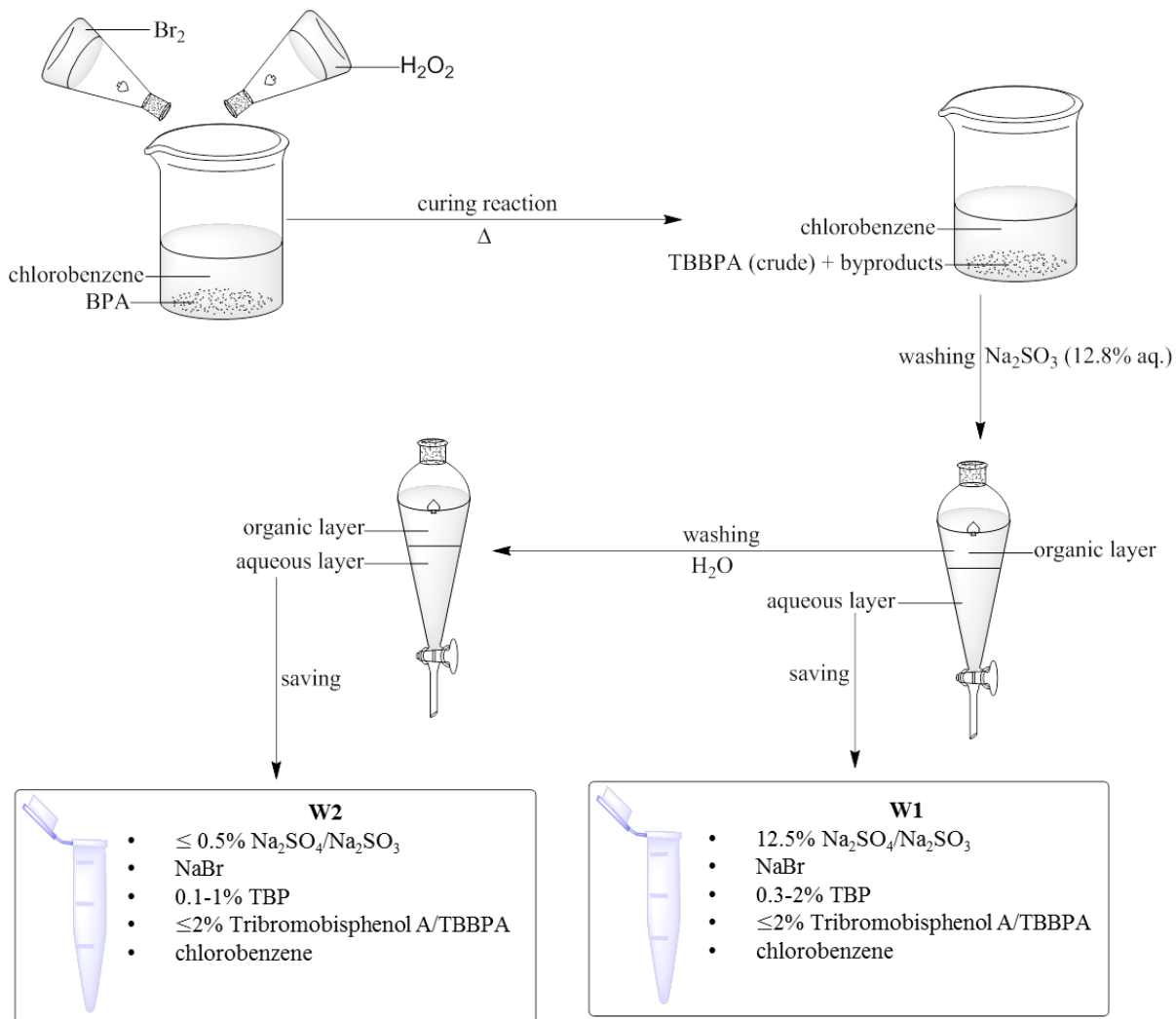


Figure 28 Schematic diagrams for TBBPA production.

Bromine and hydrogen peroxide were added to the TBBA-chlorobenzene solution at a controlled temperature. Then, the temperature of the mixture was increased until crude TBBPA was formed. Finally, the TBBPA product with high purity was obtained by successive crystallization, filtration, washing, and drying. During the TBBPA production process, multiple bromophenols (i.e., TBP, Tribromobisphenol A and TBBPA) were discarded into the outflow wastewater. There is a need for sorptive removal of discarded bromophenols from TBBPA production line. Currently, carbonaceous

adsorbent has been used for treatment of such wastewater. However, as mentioned in **Section 2.2**, carbonaceous sorbents are expensive and non-environmental friendly.

To solve the above problem, PEBA membrane was considered as an appropriate sorbent, owing to its high tolerance in acidic/basic effluents and excellent sorption capacity for bromophenols. Previous sections have studied the sorption performance of PEBA membrane for single bromophenol (i.e., BP, DBP, or TBP) solution, which was prepared in laboratory. To confirm the efficient performance of PEBA membrane on removing bromophenols in real applications, industrial effluents from TBBPA production line were used in the sorption tests.

This section will be focused on the evaluation of the sorption performance of PEBA membrane for removing discarded TBP from TBBPA industrial effluents at different conditions, including pH, temperature, adsorbent dosage, adsorbate concentration, and contact time.

5.2 Experimental

5.2.1 General Procedure for the Treatment of Bromophenols from Industrial Effluents

25 L of effluent W1 and W2 were obtained from the midstream aqueous mixtures in #1 and #5 TBBPA production line (TY-101, Weifang Binhai Economic Development Zone, Shandong, China), respectively. Prior to packaging and shipping the effluent W1 and W2 to the laboratory from the production line, the main components (mass distribution) of the sample were determined by TY (shown in **Figure 28**). The delivered industrial effluents were filtrated by using filter paper and vacuum pump to remove the insoluble contaminants left during the production period. The concentration of TBP in filtrated W1 (59 ppm) and W2 (40 ppm) were measured by UV/Vis. Consequently, the filtrated effluents were sealed under sample vials for further testing.

As shown in **Figure 28**, both W1 and W2 effluents contained TBP, which would be adsorbed by PEBA membrane sorbent. To evaluate the sorption performance of PEBA membrane for the obtained effluents, the percentage of TBP removal, defined below, was used.

$$TBP\ removal = \frac{C_0 - C_t}{C_0} \times 100\% \quad (23)$$

where C_0 is the initial concentration (mmol/L) of TBP; and C_t is the concentration (mmol/L) of TBP in the wastewater at time t (min), which was determined by using UV-Vis spectrophotometer.

5.2.2 Effects of Solution pH

The batch sorption experiments were introduced here. 1.0 g of the PEBA membrane (thickness: $200 \pm 10 \mu\text{m}$) was placed in a 250 mL Erlenmeyer flask. 150 mL of the aqueous solution of W1 and W2 with given concentrations (C_0) and different initial pH values (2, 4, 6, 8, 10, 12) were then dispensed into each flask. The pH values of W1 and W2 were adjusted with HCl and NaOH, and determined by using a pH meter. For each effluent, two flasks of the solution samples with smallest and largest pH values were left without PEBA membrane to serve as blanks. The Erlenmeyer flasks were consequently sealed with parafilm and placed in the constant temperature shaker at a pre-set temperature (298 K). The above flasks were continuously shaken at 100 r/min for a period of 24 hours, to allow for equilibration of the sorption process. Finally, the concentrations of W1 and W2 for varying initial pH values were determined with the UV/Vis spectrophotometer at corresponding λ_{max} , and TBP removal were calculated by **Equation 23**.

5.2.3 Effects of Temperature

Sorption experiments were conducted similar to those mentioned in **Section 5.2.2**, except that, the filtrated effluents W1 and W2 were dispensed into each flask without pH adjustment, and the prepared samples were shaken at 298 – 328 K with 10 K increments.

5.2.4 Effects of Adsorbate Concentration

Sorption tests were conducted with effluents at different concentrations. The stock solutions of effluent W1 and W2 were successively diluted to 90%, 80%, 70%, and 60% of their original concentrations. In addition, all sealed samples were continuously shaken at the same temperature (298 K) and the bromophenols removal at different concentrations was evaluated.

5.2.5 Effects of Contact Time

Instead of shaking the prepared samples at different temperatures for 24 hours in **Section 5.2.3**, the sealed solution with same concentration for each group were shaken at a constant temperature (298 K) for varying time (2, 5, 10, 20, 30, 40, 50, 60, and 90 min).

5.2.6 Effects of Adsorbent Dosage

The prepared PEBA membrane (thickness: $200 \pm 10 \mu\text{m}$) was cut to pieces of different masses (1.0, 0.8, 0.6, 0.4, and 0.2 g), and the sorption tests were carried out at 298 K for 24 hours.

5.2.7 PEBA Membrane Regeneration

Regeneration of PEBA membrane for TBP sorption from both effluents W1 and W2 were conducted, the PEBA membrane samples (mass: 1.0 g; thickness: $200 \pm 10 \mu\text{m}$) were immersed into the effluent for 3 hours for sorption, followed by immersion in deionized water and ethanol (99.5% v/v) for 3 hours to induce desorption. Both processes were performed at constant temperature (298 K) in a constant temperature shaker. The membrane samples were then dried in a vacuum oven and the percent desorption was determined. The same membrane was consequently used for subsequent sorption /desorption cycles to evaluate the regeneration performance.

5.3 Results and Discussion

5.3.1 Effects of Solution pH, Temperature, Adsorbate Concentration, Contact Time, and Adsorbate Dosage

Figure 29 shows that the percent TBP removal decreases with an increase in pH. This is an agreement with our previous study. A change in solution pH led to a change in solute solubility, and this affects the adsorption performance significantly.

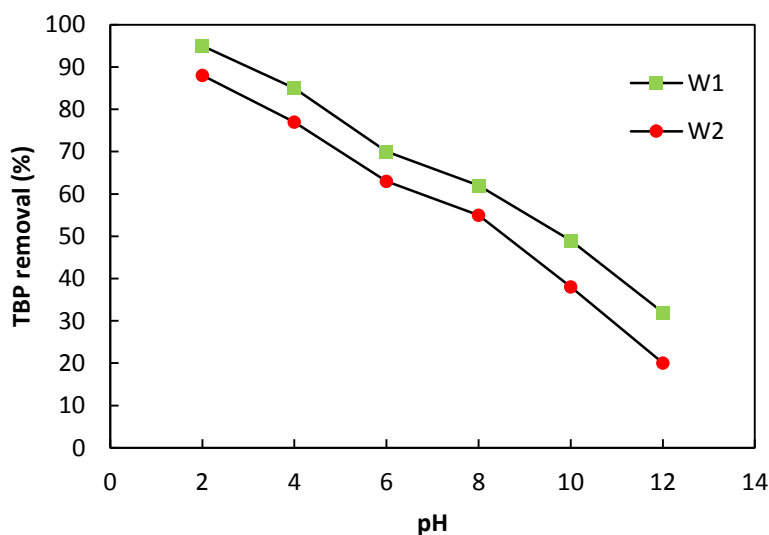


Figure 29 Effects of solution pH on the removal of TBP in TBBPA industrial effluents.

(mass of PEBA = 1.0 g; sorption time = 24 hours; temperature = 298 K; initial concentration = 59 ppm for W1, 40 ppm for W2)

Ashraf et al. [70] investigated the use of white radish peroxidase for sorptive removal of contaminated phenolic compounds from wastewater at different pHs, and the results revealed that as the pH increased from 2 to 10, the percent phenolic compound removal increased and then decreased. Obviously the effect of pH on sorption performance depends on the properties of the sorbent and the solute.

Figure 30 shows how the temperature affected TBP removal for both effluents. As expected, the sorption of bromophenols from the effluents was also an exothermic process. At 298 K, TBP removal rates for W1 and W2 were 90% and 87%, respectively. In practice, the operating temperature was determined by the mainly process operating conditions.

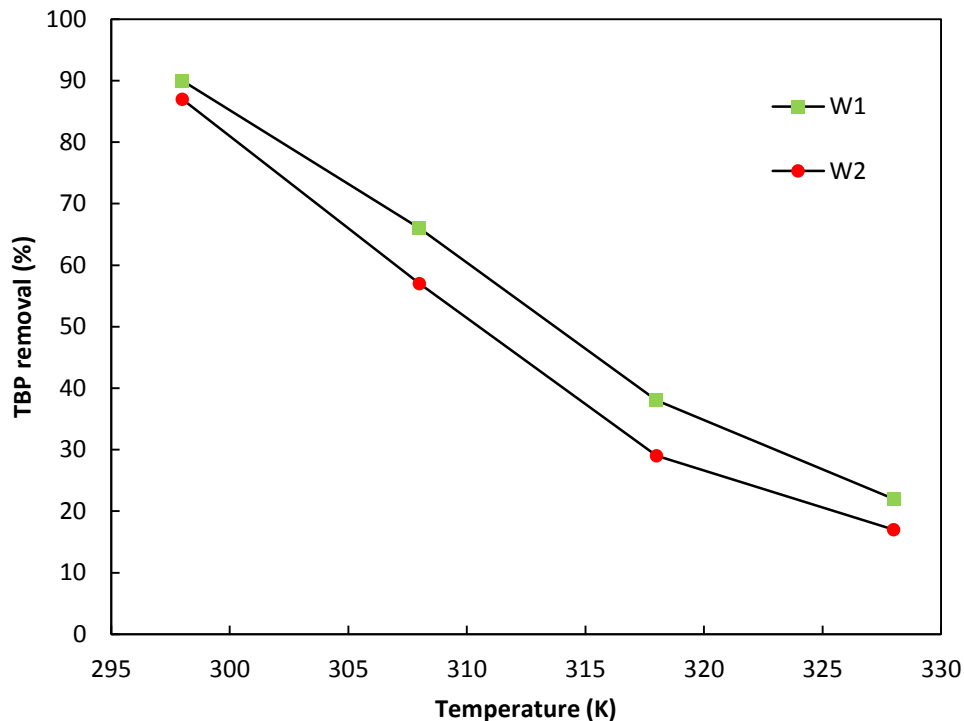


Figure 30 Effects of temperature on the removal of TBP in TBBPA industrial effluents.

(mass of PEBA = 1.0 g; sorption time = 24 hours; pH = 7; initial concentration = 59 ppm for W1, 40 ppm for W2)

Figure 31 shows the removal of bromophenols from the effluents at different concentrations. The percentage removal of TBP becomes lower at lower TBP concentrations in water. This is understandable, because the driving force for phenol sorption will be reduced when the feed is diluted, resulting in reduced sorption uptake.

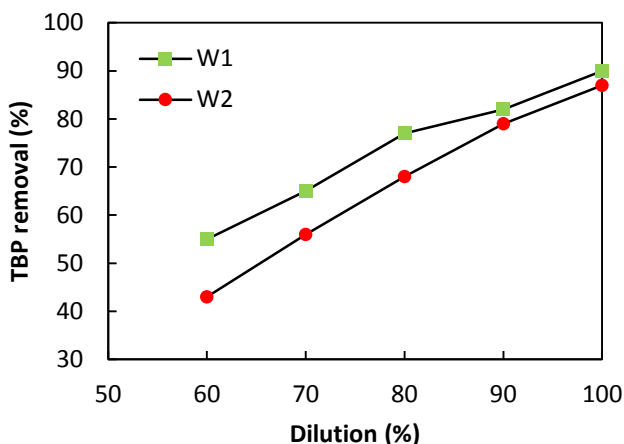


Figure 31 Effects of adsorbate concentration on the removal of TBP in TBBPA industrial effluents.

(mass of PEBA = 1.0 g; sorption time = 24 hours; temperature = 298 K; pH = 7; initial concentration = 59 ppm for W1, 40 ppm for W2)

Figure 32 shows the impact of sorption time on TBP removal. As expected, for both effluent W1 and W2, when contact time increased, the removal of TBP increased. The sorption uptake no longer changes when the contact time is long (>40 mins). This is expected, because TBP sorption on the PEBA membrane will eventually reach equilibrium, and removal percent will be a constant. Idris [40] also studied the effect of contact time on the percent sorptive removal of phenolic compounds from liquids using silica gel sludge. The results showed that the percent phenol removal continuously increased on increasing the contact time, and no further enhancement was observed after 120 mins, which was similar to the results obtained in this section. Therefore, selecting appropriate contact time was necessary for increasing sorption efficiency and lowering labor cost.

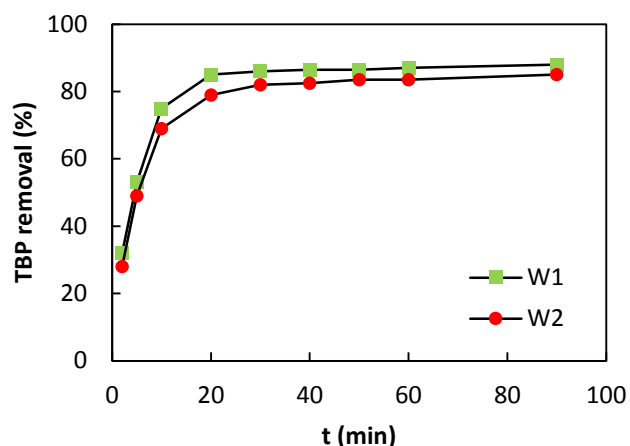


Figure 32 Effects of contact time on the removal of TBP in TBBPA industrial effluents.

(mass of PEBA = 1.0 g; temperature = 298 K; pH = 7; initial concentration = 59 ppm for W1, 40 ppm for W2)

The effects of PEBA membrane dosage on the sorptive removal of bromophenols were shown in **Figure 33**. The percent TBP removal increased with an increase in adsorbent dosage. This is obvious, because for a given effluent concentration, increasing the sorbent amount will increase the TBP uptake, resulting in an increase in the TBP removal.

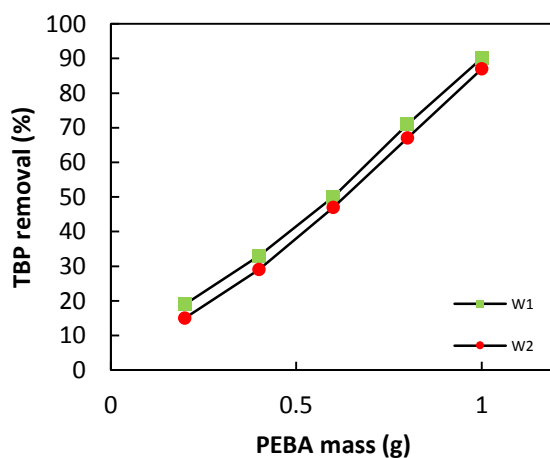


Figure 33 Effects of adsorbent dosage on the removal of TBP in TBBPA industrial effluents.

(sorption time = 24 hours; temperature = 298 K; pH = 7; initial concentration = 59 ppm for W1, 40 ppm for W2)

5.3.2 PEBA Membrane Regeneration

In order to evaluate the regeneration performance of PEBA membrane, the polymeric sorbent saturated with different bromophenols was run consecutive batch sorption and desorption tests. The fractional desorption of TBP from PEBA membrane in different solution (e.g., water, and ethanol) was depicted in **Table 13**. The percentage of TBP removed from the PEBA sorbent in ethanol was higher than that in water, which suggested that alcohols were more effective for stripping the sorbed TBP from PEBA sorbent. **Table 13** also shows that the fractional desorption was still high (> 90%) after three sorption & desorption cycles. The above results confirmed the possibility of reusing the PEBA membrane for treatment of wastewater from TBBPA industry.

Table 13 Desorption of TBP from PEBA membrane using water and ethanol after consecutive sorption and desorption process.

Effluent	Regenerative Agent	Number of Sorption Run	Desorption Rate (%)
W1	Water	1	96
		2	92
		3	91
	Ethanol	1	97
		2	93
		3	91
W2	Water	1	96
		2	93
		3	90
	Ethanol	1	98
		2	95
		3	92

5.4 Conclusions

1. The sorption potential of PEBA membrane was demonstrated for the removal of TBP from TBBPA industrial effluents.
2. The sorption studies with two industrial effluent samples showed that a lower pH and temperature favored TBP removal.
3. The PEBA membrane was reusable for treatment of wastewater from TBBPA industry.

Chapter 6

General Conclusions and Recommendations

6.1 General Conclusions

PEBA was studied as a promising material to adsorb bromophenol. The sorption of several bromophenols (i.e., BP, DBP, and TBP) onto PEBA membranes and pellets was investigated.

The sorption isotherms of the three bromophenols on PEBA were determined. The effects of temperature and pH on sorption performance were investigated. The sorption seems to be an exothermic process, and the sorption isotherms of BP, DBP, and TBP obeyed both the Langmuir and Freundlich models. The sorption capacity of PEBA for the bromophenols was analyzed based on the fitted models, and the solubility of bromophenols in water was correlated to the sorption capacity of the phenols in the PEBA membrane.

The effects sorbate concentration and temperature on the sorption kinetics of the three bromophenols onto PEBA membrane were studied. The rate of sorption of BP, DBP, and TBP onto PEBA membrane followed the pseudo-second order kinetics model, and diffusion was not the dominating mass transfer mechanism during the sorption process.

The application of PEBA membrane in treating industrial effluents from TBBPA production was demonstrated. The potential of using PEBA membrane for the removal of discarded TBP from the industrial effluents was evaluated. The effects of pH, temperature, solute concentration, sorption time, and sorbent dosage on the percent TBP removal were tested. In addition, studies on the regeneration and reuse of PEBA membranes for repeated uses for TBP removal were carried out, confirming feasibility of using PEBA to treat effluents from TBBPA production.

6.2 Recommendations

6.2.1 Further Thermodynamic Studies

Preliminary isotherm results using PEBA membrane as sorbent were presented in **Chapter 3**. The next step would be to do the thermodynamic studies and to determine the thermodynamic parameters (i.e., Gibbs energy, enthalpy and entropy changes in the sorption process), which may also support the sorption process was exothermic.

6.2.2 Modification of the Pseudo-Second Order Kinetics Model

As mentioned in **Chapter 4**, the sorption of all three bromophenols in PEBA membrane obeyed the pseudo-second order kinetics model. In the data fitting, the value Q_e was assumed constant to calculate the parameters based on the linearized isotherm plots. In fact, the value of Q_e changes with instant adsorbate concentration during the sorption process. Thus, further modification of the pseudo-second order kinetics model data fitting is necessary to obtain more accurate kinetic parameters to get a deeper insight into the sorption mechanisms.

6.2.3 Further Regeneration Studies

Preliminary work on PEBA regeneration using deionized water and ethanol (99.5% v/v) as regenerative agents were done in **Section 5.3.2**. Further investigation on optimization of the regeneration methods (e.g., temperature, use of vacuum, or using other regenerative agents) for better regeneration performance is needed.

Appendix A

UV/Vis Absorption Spectrum of Bromophenols

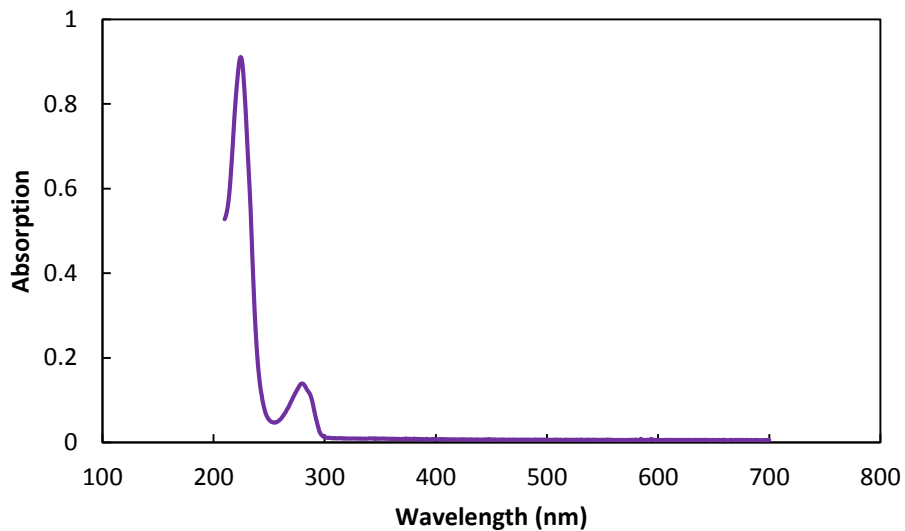


Figure A. 1 UV/Vis absorption spectrum for 100 ppm BP solution. (T = 298 K)

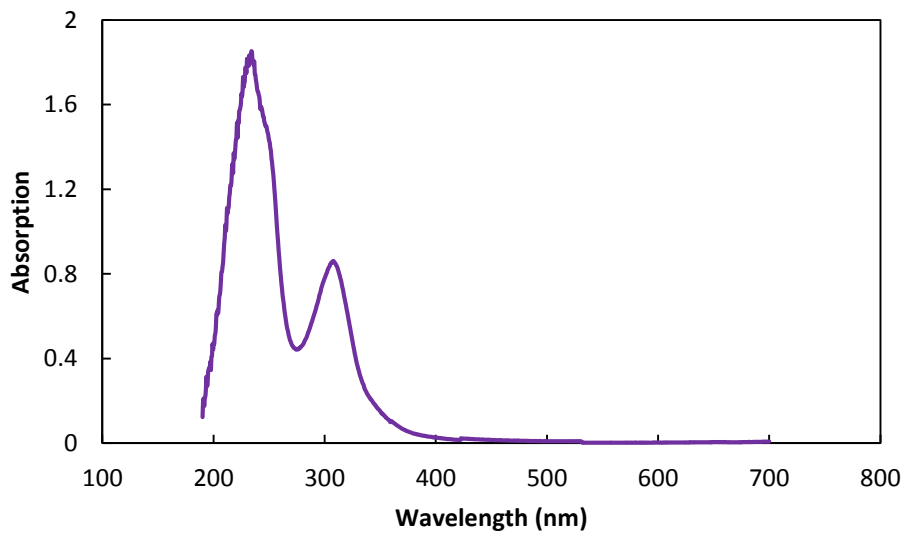


Figure A. 2 UV/Vis absorption spectrum for 50 ppm DBP solution. (T = 298 K)

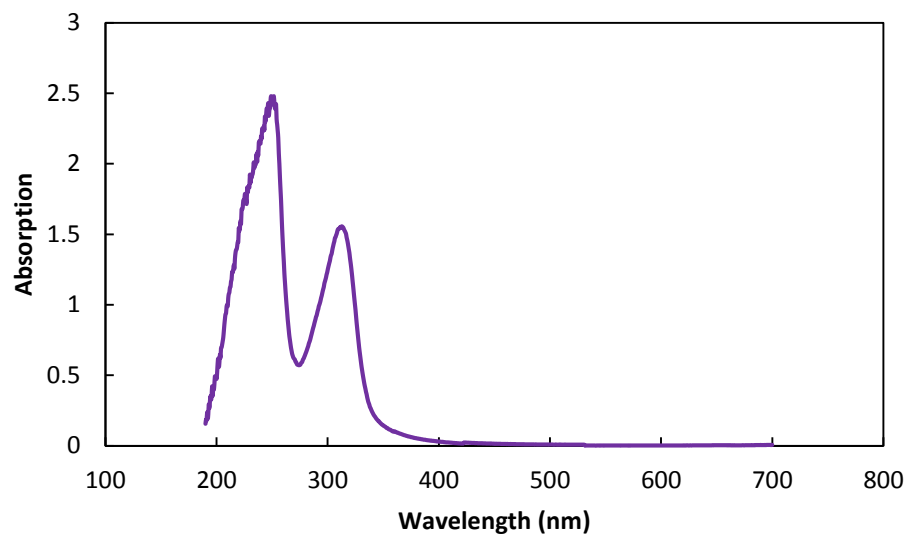


Figure A. 3 UV/Vis absorption spectrum for 50 ppm TBP solution. (T = 298 K)

Appendix B

Calibration Curves for Estimating Concentration of Bromophenols

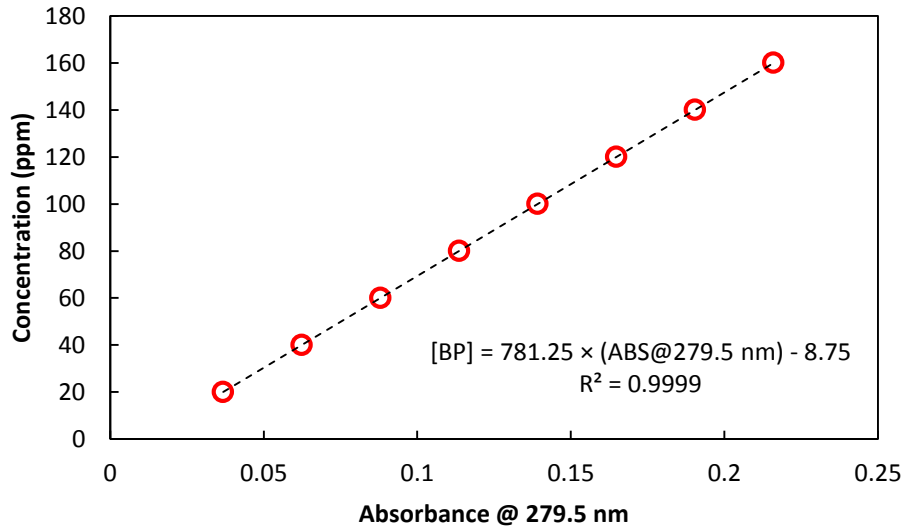


Figure B. 1 UV/Vis spectrophotometer calibration curve for BP solution from 20 - 160 ppm.

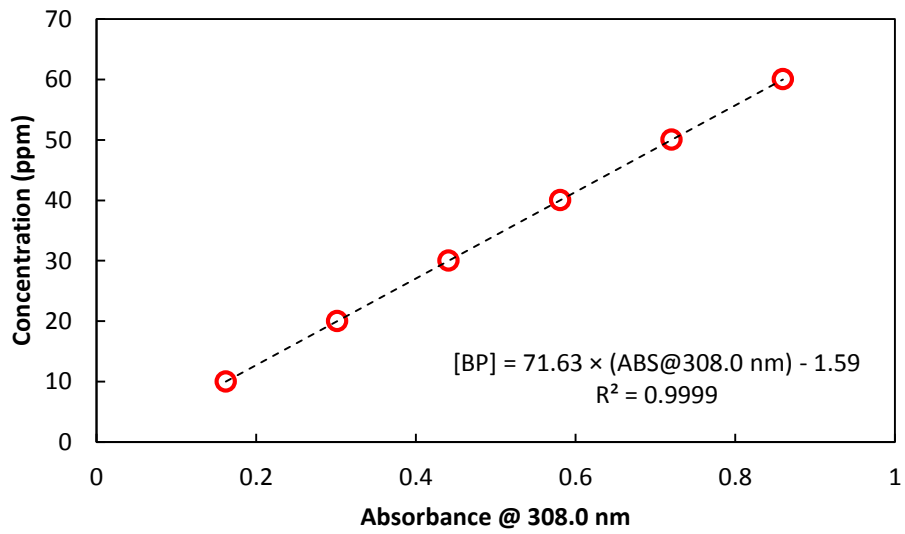


Figure B. 2 UV/Vis spectrophotometer calibration curve for DBP solution from 10 - 60 ppm.

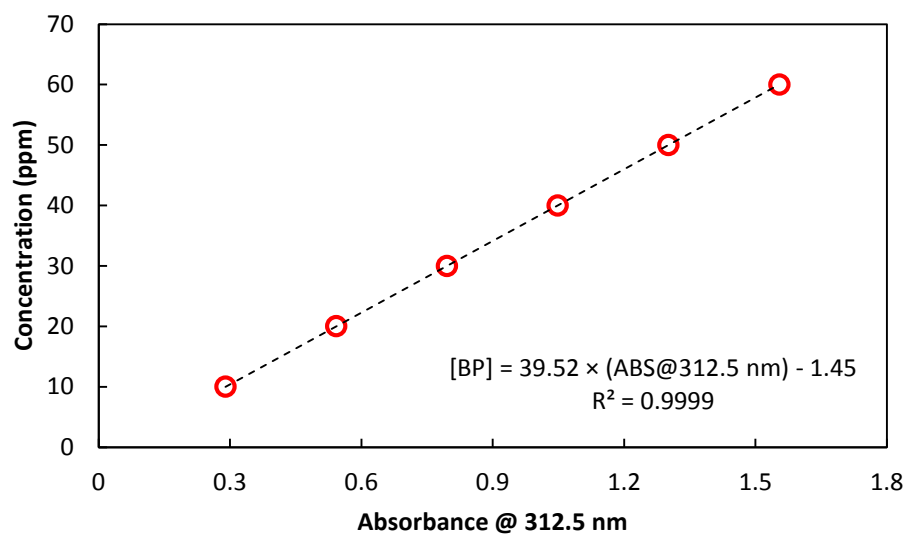


Figure B. 3 UV/Vis spectrophotometer calibration curve for TBP solution from 10 - 60 ppm.

Appendix C

UV/Vis Absorption Spectrum of Effluents from TBBPA Production

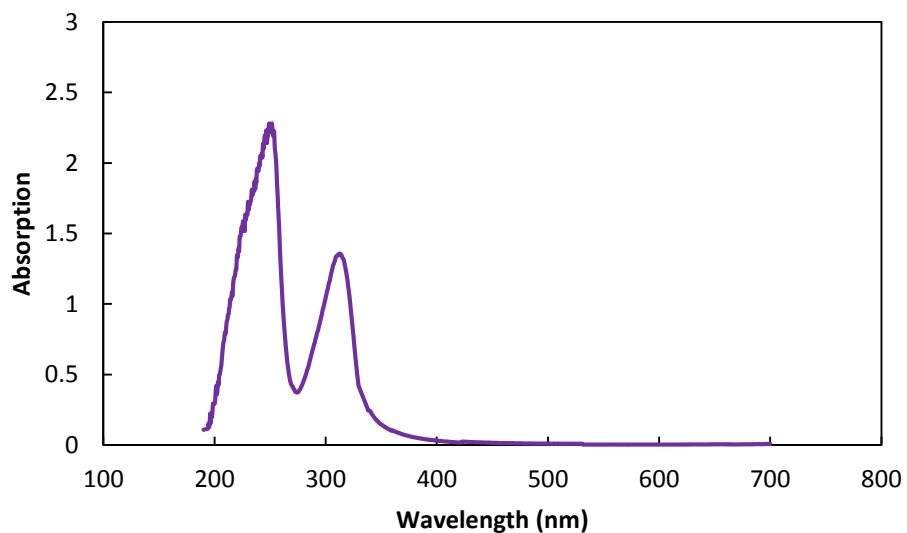


Figure C. 1 UV/Vis absorption spectrum for effluent W1. (T = 298 K)

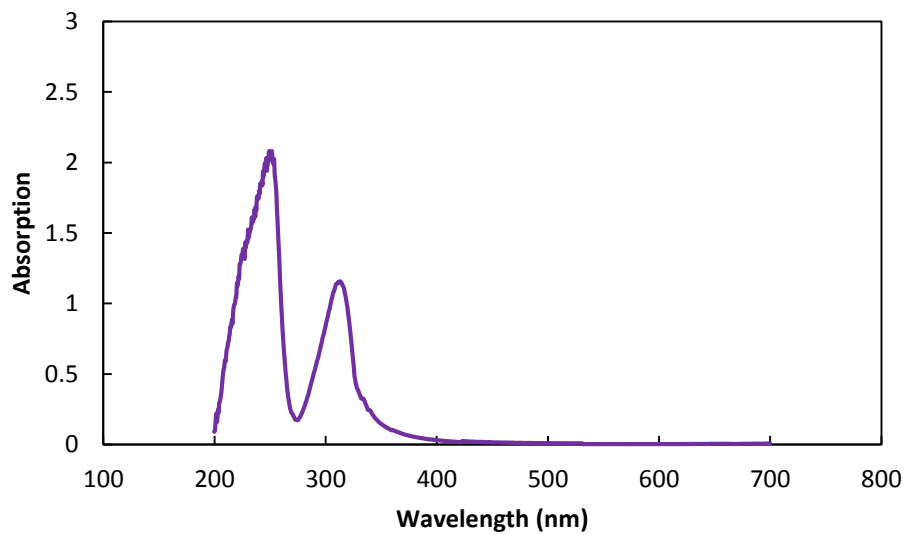


Figure C. 2 UV/Vis absorption spectrum for effluent W2. (T = 298 K)

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