BATCH ADSORPTION OF BISPHENOL A (BPA) ON COCONUT SHELL ACTIVATED CARBON

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by

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ABSTRAK

Masalah pencemaran air yang disebabkan oleh bahan cemar yang muncul atau dengan kata lain sisa organik seperti sisa Bisfenol A (BPA) yang ditemui dalam aliran air sisa semula jadi semakin teruk baru-baru ini. Hal ini juga dianggap sebagai salah satu sebatian pengganggu endokrin yang boleh mengancam kesihatan manusia dan biasanya terdapat dalam sumber - sumber air. Dalam kajian ini, siri eksperimen dalam penjerapan kelompok BPA pada karbon teraktif tempurung kelapa telah dijalankan untuk menyiasat sifat penjerapan BPA pada pelbagai parameter seperti kepekatan awal BPA, suhu serta dos penjerap. Karbon teraktif tempurung kelapa mempunyai julat saiz liang 0.425 hingga 0.152 mm. Kapasiti penjerapan maksimum, Q_m ialah 279.5864 mg/g pada 50 °C. Selain itu, model kinetik pseudo-tertib pertama mempunyai kesesuaian yang lebih baik dengan data eksperimen. Dari segi termodinamik, penjerapan BPA pada karbon teraktif tempurung kelapa dikenal pasti sebagai proses spontan dan eksotermik secara semula jadi. Bagi profil penjerapan BPA adalah yang terbaik dipadankan dalam model garis lengkuk sesuhu Langmuir, menunjukkan bahawa penjerapan satu lapisan pada tapak aktif penjerap sambil mengalami permukaan homogen pada permukaan penjerap. Oleh itu, mengikut keputusan garis lengkuk sesuhu, kinetik dan termodinamik, kita boleh merumuskan bahawa penjerapan BPA pada tempurung kelapa karbon diaktifkan mengikut mekanisma penjerapan secara fizikal.

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ABSTRACT

The problem of water contamination caused by emerging contaminant (EC) or in other words organic residue like Bisphenol A (BPA) residues found in natural wastewater streams has recently gotten a lot worse. This EC also being considered as one of the endocrine-disrupting compounds (EDC) that may threaten human health and usually found in the water bodies. In this study, series of experiments in batch adsorption of BPA of coconut shell activated carbon were conducted to investigate the adsorption properties of BPA at various parameters such as initial concentrations of BPA, temperatures as well as adsorbent dosage. The coconut shell activated carbon had a pore size range of 0.425 to 0.152 mm. The maximum adsorption capacity, Q_m was 279.5864 mg/g at 50 °C. Moreover, the pseudo-first-order kinetics model possessed a better fit to the experimental data. In terms of thermodynamic, the BPA adsorption on the coconut shell activated carbon was identified as spontaneous and exothermic process in nature. As for the adsorption profile of BPA was the best fitted in the Langmuir isotherms model, suggesting that monolayer adsorption on the active sites of the adsorbent while experiencing the homogenous surface on the adsorbent's surface. Therefore, according to the isotherm, kinetic and thermodynamic results, we could summarize that the BPA adsorption of coconut shell activated carbon following the physisorption mechanism.

CHAPTER 1

INTRODUCTION

1.1 Emerging Contaminant (EC) and Endocrine Disruptors Compound (EDC)

Pesticides and fertilizers, pharmaceutical, personal care products, fragrances, plasticizers as well as flame retardant are the example of emerging contaminants (EC). EC are also known as emerging pollutants (EP). They disperse in the environment due to the excessive and strong use in industry. They are widely available in different class and types. EC or micropollutant usually produced by various sources such as synthetic and natural substances as reported by Arman et al., (2021). Any compound of manufactured or natural source or any microorganism that is not commonly detected in the surrounding but might potentially create unfavorable environmental and human health effects is the main concern of EC defined by the US Geological Survey. EPs are substances that can persist in the environment, bioaccumulate, and pose a risk to human health, such as causing abnormal growth, decreased fertility and reproductive health, neurodevelopmental delays, inhibiting wildlife species, degrading aquatic ecosystems, and potentially harming the human immune system. According to Sivaranjanee and Kumar, (2021), these contaminants are typically released in water bodies and only a trace amount of part per trillion or per billion usually be found. The majority of emerging contaminants are not new or newly introduced pollutants into the environment, which is important to note. On the other hand, most emerging contaminants are well-known pollutants with a newly proven detrimental effect or method of action. As a result, the term "emerging" refers to both the pollutant and the problems that have contributed to the evolution of it. The EC groups and their main constituents are listed in Table 1.1.

Table 1. 1 Groups of emerging contaminants and their key constituents (Arman *et al.*, 2021)

Groups	**Example**	**Compound**
Pharmaceuticals	Human antibiotics and veterinary	Trimethoprim, erytromycine, amoxicillin, lincomycin, sulfamethaxozole, chloramphenicol
	Analgesics, anti-inflammatory drugs	Ibuprofene, diclofenac, paracetamol, codein, acetaminophen, acetylsalicilyc acid, fenoprofen
	Psychiatric drugs	Diazepam, carbamazepine, primidone, salbutamol
	β-blockers	Metoprolol, propanolol, timolol, atenolol, sotalol
	Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid, etofibrate, gemfibrozil

	X-ray contrasts	Iopromide, iopamidol, diatrizoate
Personal care products	Fragrances	Nitro, polycyclic and macrocyclic musks, phthalates
	Sun-screen agents	Benzophenone, methylbenzylidene camphor
	Insect repellents	N,N-diethyltoluamide
Endocrine Disrupting Chemicals (EDCs)		4-octylphenol, cholesterol, estrone, 17β-estradiol, 17α-ethinylestradiol, coprostanol, progesterone, stigmasterol, 4-nonylphenol, Di(2-ethylhexyl) phthalate (DEHP), Bisphenol A (BPA)
Flame retardants		Polybrominated diphenyl ethers (PBDEs): polybromonated biphenyls (PBBs) – polybromonated dibenzo-p-dioxins (PBDDs) –polybromonated dibenzofurans (PBDFs),

	Tetrabromo bisphenol A, C10-C13 chloroalkanes, Tris (2-chloroethyl) phosphate, Hexabromocyclododecanes (HBCDs), Hydrophobic Brominated Compounds
Plasticizers	Di-2-propylheptyl phthalate (DPHP), Di-2-ethylhexyl terephthalate (DEHTP), Di-n-butyl adipate (DnBA), Di-isobutyl adipate (DIBA), Di-iso-nonyl adipate (DINA)

Endocrine Disruptors Compound (EDC) is one of EC that has gain serious attention from the community due to its dangerous effect on human. Manufactured products are where EDC can be usually found. EDC also xenobotics compound that comprises of particularly plastic bottles, children’s toys and PVC pipes. EDCs are a group of compounds that have an effect on wildlife and humans' sexual development, reproduction, and endocrine systems, even at very low concentrations. They are usually discharged into wastewater treatment plants (WWTPs) and then released into the aquatic environment without any risk evaluation (Su *et al.*, 2020). The exposure of EDC is harmful as it can bind to body endocrine receptors to alter, activate and mimic the natural hormone synthesis. False hormonal signal as a result from the above EDC works biologically could give false hormonal signals that would eventually increase, decrease or inhibit function of the normal endocrine function.

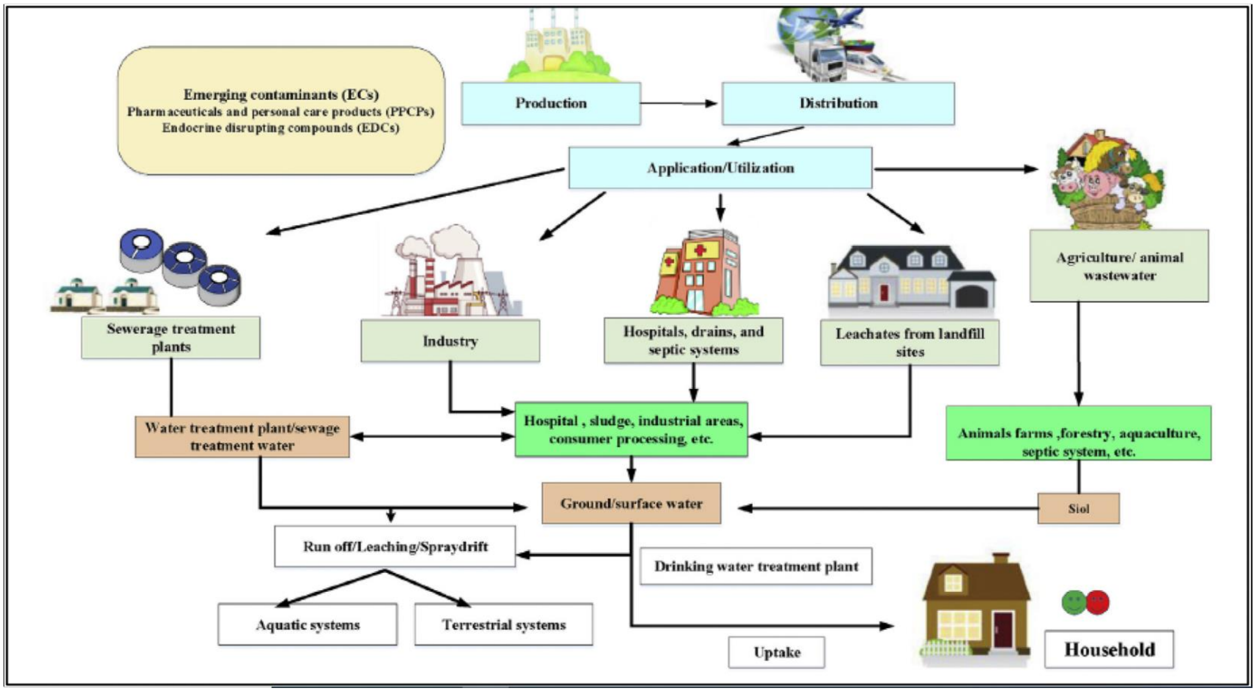


Figure 1. 1 Sources and pathways of ECs (D. Yadav *et al.*, 2021)

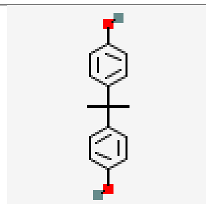
Figure 1.1 shows that ECs consist of pharmaceutical and personal care products (PPCPs) as well as EDC contaminate the soil, water, and air through a variety of mechanisms and applications, damaging both the environment and human health. This phenomenon should be stopped to avoid continuously threatening both environment and human health.

1.2 An insight of Bisphenol A (BPA)

Bisphenol A (BPA) is an EDC that is widely used in the production of plastics, resins, and other materials (Wang et al., 2019). Kouidhi et al., (2017) reported that in vitro and in vivo studies have demonstrated that BPA possesses estrogenic characteristics. In reality, BPA can bind to the estrogen receptor (ER) and a variety of other hormone receptors, including the androgen receptor, thyroid hormone receptor, and peroxisome proliferator-activated receptor- γ (PPAR). The exposure of BPA to human health is an undeniable threat as the biological reproductive could be disrupted. Therefore, in the first place, it is important to remove BPA efficiently.

Additionally, BPA is used extensively in industry, such as in the production of polycarbonate, epoxy resins, and PVC stabilizer. On a global scale, approximately 65% of BPA is used in the production of polycarbonate, 25% in the production of epoxy resins, and 10% in the production of other substances. BPA is also utilized in foods and cosmetics as an antioxidant (Tomza-Marciniak *et al.*, 2018). In terms of the uses, BPA contains in polycarbonate plastics are extremely durable and reliable. They can tolerate high temperatures, allowing them to be used in microwave ovens, and they can withstand high-impact crashes, making them essential as parts of safety equipment such as safety glasses, face protectors, motorcycle helmets, and bullet-resistant windows. BPA extends the shelf life of food and beverage goods by acting as a component of epoxy resins in protective coatings such as those that cover the inside surfaces of cans (Kara Rogers, 2021). The molecular properties of BPA or 4, 4'-(Propan-2-ylidene) Diphenol can be represented in table 2.1.

Table 1. 2 Molecular properties of BPA

Molecular structure (2D)	Molecular formula	Molecular weight
	$C_{15}H_{16}O_2$ or $(CH_3)_2C(C_6H_4OH)_2$	228.29 g/mol

Due to its nature as one of the endocrine-disruptors chemicals, it is an urge to remove the eluted BPA effectively in any water bodies such as waste landfill leachates, rivers, seas and soil. BPA is also found in varying quantities in many types of water. For example, hazardous waste landfill leachate contains 17.2 mg/L, stream water contains 12 µg/L, drinking water contains between 3.5 and 59.8 ng/L, and polycarbonate factory effluents include around 100 mg/L (Martín-Lara *et al.*, 2020). According to Chang et al., (2012) membrane filtration, biological process, oxidation process and adsorption process were identified as conventional methods that responsible for the removal of EDCs. However, it is found that the adsorption process using activated carbon is the most eco-friendly and frequently utilized for the elimination of EDCs among the several clean-up techniques available (Chang *et al.*, 2012). The effects of BPA are tabulated in Table 2.2 below.

Table 1. 3 EDC effects mainly BPA

Endocrine Disrupting Component (EDC)	**Effects**	**References**
BPA	Causes damage to brain structures, thyroid glands, and reproductive organs in children, and it has recently been linked to the development of cancer in humans.	(Chouhan *et al.*, 2014)
	BPA exposure during pregnancy and childhood may be linked to altered neurodevelopment and obesity.	(Braun and Hauser, 2011)
	EDCs influence creating hypothalamic neuroendocrine frameworks	(Gore, Krishnan and Reilly, 2019)

1.3 Activated Carbon Adsorption

Various treatments are suggested by Sivaranjanee and Kumar, (2021) such as ion exchange, adsorption, reverse osmosis, chemical reduction, hydrolysis, chemical oxidation, precipitation, filtration and flotation. The adsorption process offers considerable advantages over the other techniques to remove EC particularly bisphenol A (BPA) since it is effective, versatile, efficient, and simple to use, and it requires little energy (Sivaranjanee and Kumar, 2021). In recent years, the sorption technique using waste, artificial, or vital materials for the expulsion of developing pollutants has been discussed. Activated carbon (AC) is a regularly used sorbent because of its high explicit surface zone and porosity. For usage as adsorbents, AC is porous, affordable, and easily available, providing a large surface area to remove pollutants. It has higher usable surface area per grams (between 500-1000 m^2/g) than any other physical adsorption material (Lenntech, 2022). Moreover, AC are very adaptable industrial adsorbents that are utilised in a wide range of applications involving the removal of unwanted species from liquids or gases by adsorption in order to achieve purification or the recovery of chemical contents. In fact, AC, in particular, have excellent adsorbent properties: high porosity and surface area (about 3000 m^2/g), high degree of surface reactivity, and a wide range of surface chemical properties as reported by Martín-Lara et al., (2020). Hence, making it suitable as an adsorbent.

A previous study by Martín-Lara et al., (2020) fixed the temperature at 25 ℃ while varying the adsorbent dose, contact time and in order to study the adsorptive behavior of activated carbon in removing BPA. In contrast, this study is proposed to fix the solution at certain pH while varying three parameters which are adsorbent dosage, initial concentration of BPA and temperatures. We also use activated carbon as an adsorbent in completing this study. Besides, Liu, Li and Campos, (2017) emphasize that activated carbon is now widely used in drinking water advanced treatment processes and point-of-use filter systems to remove pollutants such as halogenated nitrogenous disinfection by-products, natural organic matter (NOM), taste and odor, bacteria, and other contaminants.

1.4 Problem Statement

The presence of BPA in water bodies mainly comes from industrial wastewater particularly in polycarbonate, epoxy resins or plastics industry. The increasing demands of these products lead to an increase in the BPA production of 64% in conjunction with epoxy resins and polycarbonate production in 2018. BPA is also known as one of the EC or EDC that we are looking forward to eliminating this hazardous chemical before releasing the industrial wastewater to any water bodies. EDC is very harmful to humans and animals, mainly aquatic life in general. As for humans, EDC can mimic natural hormones as well as alter the hormone receptors when high doses of EDC bind to the receptors is unacceptably harmful. This is because exposure to EDC could alter the regulation of hormones, contribute to fertility damage, reproductive disorders due to its carcinogenic effect. The aquatic life and ecosystem will also be greatly affected by the untreated wastewater effluent from the industries. It is considered harmful to marine life when 1000 to 10 000 µg/L of EDC concentration are detected in the water bodies (Mpatani *et al.*, 2021). Nevertheless, estrogenic activity can occur even when the concentration is lower. High-quality surface water and groundwater, and drinking water are expected when BPA or EDC manages to be removed efficiently. However, achieving those at high quality is nearly impossible when using inappropriate clean-up techniques. Currently, various clean-up techniques were suggested by Chang et al., (2012) such as membrane filtration, biological processes and adsorption. Adsorption by using activated carbon as an adsorbent is the best among the clean-up methods as it is ecologically friendly, simple, cost-effective due to its low investment and does not create the second pollution. Activated carbon is one of the well-known adsorbents associated with a porous surface that can enhance the adsorption of the contaminant due to its large surface area provided. Hence, this study intended to study the adsorption behavior of BPA onto activated carbon at fixed pH while varying other parameters such as temperature, initial concentration of BPA and adsorbent dosage in batch mode. From the experimental data obtained, further analysis is needed in order to study the adsorption isotherms, kinetics and thermodynamics eventually understand the adsorption process well.

1.5 Research Objectives

i) To study the effect of adsorbent dosage, initial concentration of BPA and temperature at fixed pH on the BPA adsorption on coconut shell activated carbon.

ii) To compare the behavior of BPA adsorption by using adsorption isotherms and adsorption kinetics model.

iii) To investigate the thermodynamics properties of the Gibb’s free energy, the enthalpy, the activation energy and the entropy.

CHAPTER 2

LITERATURE REVIEW

2.1 Clean-up Techniques in Removing EC

There are various clean-up techniques to remove EC from water bodies. One of the methods is by membrane technology. According to Norfazilah, Ismail and Umairah Mokhtar, (2020), non-biological and biological type of membrane technologies are being used by the industry. Reverse osmosis, ultrafiltration and nanofiltration are non-biological membrane technologies. They require high pressure across membrane to facilitate filtration process. It is common process if membrane technologies are applied. Besides removing microbiological contaminants or other EC from water bodies, turbidity is also being removed along with the membrane technology used. As for biological membrane technology, membrane bioreactor technology (MBR) is used. This type of bioreactor combines both ultrafiltration or microfiltration with suspended growth biological reactor. This method can be classified as prominent and proven process in producing clean water from EC these days. However, putting aside their ability to remove EC and other pollutants efficiently, this method also has some drawbacks. It includes high cost is needed if want to apply in large scale; industrial scale. Fouling issues tend to arise when dealing with membrane technology and may causes interruption during treatment process. This phenomenon could be worsened if the feed is high in acidity or ionic strength led to increase in fouling.

Other than membrane technology, biological treatment also can be carried out in removing EC. It is a secondary treatment that consists of activated sludge process (ASP) and trickling filter (TF). ASP mainly treats industrial and domestic water. The presence of aerobic bacteria and other microorganism making this treatment is feasible for EC removal. Theoretically, sufficient amount oxygen is required in order to continue and carry out the treatment process. Reactor, separator and recycle are the basic and main part for ASP to operate. Thus, only small space is required for biological treatment. Nevertheless, this whole treatment demands high energy as well as the changes of the effluent characteristics are rigid limits this treatment to be avoided at the first place.

Taking into considerations of the limitations and drawbacks for both clean-up techniques above, adsorption process is selected due to several outstanding it could provide. Adsorption is the mass transfer of substances between two phases, such as a liquid-liquid interface, a liquid-solid interface, a gas-liquid contact, or a gas-solid interface (Norfazilah, Ismail and Umairah Mokhtar, 2020). Adsorption by using activated carbon as an adsorbent is the best among the clean-up methods as it is ecologically friendly, simple, cost-effective due to its low investment and does not create the second pollution. The inexpensive and easily available adsorbent would undoubtedly make an adsorption-based approach a feasible option for the treatment of polluted wastewater. The most important component of ensuring maximum removal of different types of pollutant is selecting an appropriate adsorbent based on the adsorbent and adsorbate characteristics.

2.2 Adsorption Process

Adsorption is a mass transfer mechanism that occurs when gases or solutes adhere to solid or liquid surfaces. Owing to imbalanced forces, the molecules or atoms on the solid surface have leftover surface energy, which is referred to as adsorption. When certain substances meet with a solid surface, these uneven forces attract them, causing them to stick to the solid surface (Hu and Xu, 2019). Liquid-gas and liquid-liquid adsorption systems are two types of adsorption systems. If a liquid is an adsorbent, the interfacial layer is referred to as a film, micelle, or emulsion. The other system is solid-liquid or solid-gas; because the adsorbent is solid, the acceptable adsorption mechanism is the interfacial layer model (Alaqarbeh, 2021). The equilibrium between the adsorbent and the bulk phase is described by the interfacial layer. The substrate binds to the sorbent surface in the first region, while the sorbent's surface layer is in the second.

There are two types of adsorptions namely physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption is dominated by weak van der Waals forces; nevertheless, chemisorption can occur due to covalent bonding and electrostatic attraction (Ameri *et al.*, 2020). This indicates that chemisorption has stronger forces than physisorption. Since this type of bonding can change the chemical form of the adsorbed molecules, it is irreversible. According to Shinde, Kamble and Sunita (2020), physical adsorption occurs when a multilayer of adsorbate forms on the adsorbent. It has a low adsorption enthalpy. Meanwhile, chemisorption has a higher adsorption enthalpy due to formation of unilayer adsorbate on adsorbent. General mechanism of adsorption is described in Figure 2.1 below.

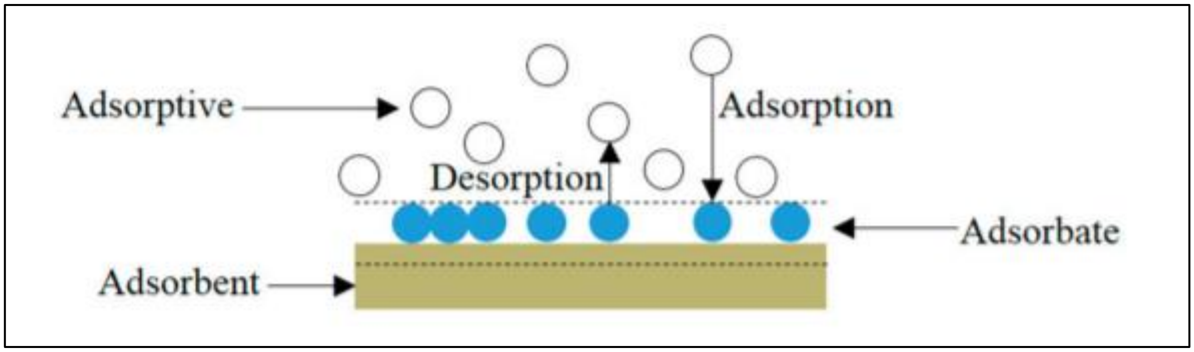


Figure 2. 1 General mechanism of adsorption *(Ameri et al., 2020)*

The mechanism of adsorption involving the movement of adsorbate from bulk phase on the surface of adsorbent, followed by the transport of adsorbate into adsorbent and finally, the adsorption of adsorbent occurs. When an equilibrium is altered on the adsorbent surface, desorption occur whereby the adsorbate will release from or through the surface of adsorbent.

2.3 Activated Carbon (AC)

Activated carbon is a coarse type of graphite with a random or amorphous structure that is highly porous over a wide range of pore sizes, from visible cracks and crevices to molecular cracks and crevices. According to Saleem et al. (2019), the pore structures of activated carbons aid in high adsorption. Because of this property, activated carbons are one of the materials used to remove organic compounds such as EC from wastewater or any water bodies. Surface areas for commercial grade carbons typically range from 500 to 1500 m^2/g, with some reaching as high as 3000 m^2/g (Saleem *et al.*, 2019). As per the IUPAC (International Union of Pure and Applied Chemistry), pores are categorized into three types depending on pore size:

i) Macropores (>50 nm diameter)

ii) Mesopores (2-50 nm diameter)

iii) Micropores (<20 nm diameter)

Micropores make up a significant portion of the interior surface area. Macro and mesopores are important for kinetics because they act as pathways into the carbon particle. They are further divided into two sub-categories based on their applications: gas phase and liquid phase, with the former being microporous (pore diameter 2 nm) in granular form (2.36–0.833 mm, or 8/20 mesh size) and the latter being mesoporous (pore diameter 2–50 nm) in powdered form (0.150–0.043 mm, or 100/325 mesh size). Activated carbons, both granular and powdered, have been found to be successful in wastewater treatment, where they play a key role in decolorization, smell removal, metal recovery, and organics adsorption (Saleem *et al.*, 2019).

2.4 Effect of Various Parameters on BPA Adsorption

One of the factors affecting the adsorption of bisphenol A (BPA) on activated carbon is the temperature of the solution. According to the adsorption principle, adsorption reduces as temperature rises, and molecules that were previously adsorbed on a surface tend to desorb from it at higher temperatures. However, for activated carbon, a different tendency is observed, in which increasing temperature reduces viscosity and enhances molecular motion, allowing molecules to enter pores more easily, leading adsorption to increase as temperature rises (Jnr and Spiff, 2005). Nevertheless, Marczewski et al., (2016) explained that adsorption is a spontaneous process that has been discovered to be exothermic in many circumstances. As a consequence, one would expect adsorption to decrease as the temperature rises. BPA as the adsorbate in this study tends to escape from the solid phase to the solution. As a result, the adsorption capacity decreases at a higher temperature. According to Le Chatelier's principle, for any physisorption, adsorption is inversely proportional to the temperature as at higher temperatures, desorption tends to occur due to the removal of adsorbates molecules (Hemant More, 2020).

Moreover, in theory, as the initial concentration of BPA rises, so does the loading capacity of activated carbon. However, the rate of BPA elimination slows down over time. According to Chang et al., (2012) when a solution contains a high concentration of BPA, the adsorbent's adsorption capacity increases, providing the necessary driving force to overcome resistance to BPA mass transfer between the aqueous and solid phases. This is because the initial concentration of BPA can influence the efficacy of BPA removal. When there is a low initial concentration of BPA in a solution, the accessible surface area to BPA concentration ratio is large, and vice versa. Of course, a larger ratio increases the likelihood of BPA elimination compared to a lower ratio.

The adsorbent dosage in terms of weight which is activated carbon is also one of the important variables or parameters to study the adsorption of BPA. Increasing adsorbent dosage leads to an increase in adsorption pores and sites (Adib *et al.*, 2017;

Kuang, Zhang and Zhou, 2020). Thus, promotes higher chances of BPA adsorption on the activated carbon. The equilibrium is achieved once the activated carbon dosage reaches a certain value. When there are too many adsorption sites and pores to facilitate the BPA adsorption process, the surface of activated carbon will reach surface equilibrium. This is because there is still vacant in adsorption sites and pores due to lack of BPA. Hence, decreasing the ability of BPA adsorption.

2.5 Adsorption Isotherms

Adsorption isotherms are another crucial part involved in the adsorption process. The adsorption isotherm is a graphical representation of the relationship between the amount adsorbed by a unit weight of adsorbent (e.g., activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium, as well as the distribution of an adsorbable solute between the liquid and solid phases at different equilibrium concentrations (Ng *et al.*, 2002). Therefore, specifically in this study, the adsorption isotherm is an empirical relationship that predicts how much BPA-activated carbon can adsorb.

2.5.1 Langmuir Isotherm

The most frequent model for quantifying the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a given temperature is the Langmuir adsorption model. The Langmuir isotherm model assumes that the adsorption process takes place at specific homogenous spots on the adsorbent's surface. Furthermore, when a molecule is adsorbed onto a site, other molecules are unable to adsorb at that site, according to the assumptions (Rezakazemi and Zhang, 2018).

Equation 2.1 below can be used to represent Langmuir Isotherm,

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{Eq. (2.1)}$$

Where K_L= Langmuir adsorption constant (L/mg)

q_m= maximum adsorption capacity (mg/g)

2.5.2 Freundlich Isotherm

The Freundlich isotherm can be used to describe adsorption processes on heterogonous surfaces. The surface heterogeneity and the exponential distribution of active sites and their energy are defined by this isotherm.

Freundlich isotherm is represented using the Equation 2.2 below,

$$q_e = k_F C_e^{1/n} \qquad \text{Eq. (2.2)}$$

Where,

K_F= adsorption capacity

n= favor of the adsorption process (mg/g (L/mg) $^{1/n}$)

2.5.3 Temkin Isotherm

The Temkin isotherm model considers the effects of indirect adsorbate/adsorbate interactions on the adsorption process, as well as the assumption that the heat of adsorption (ΔH_s) of all molecules in the layer reduces linearly as surface coverage increases (Ayawei, Ebelegi and Wankasi, 2017).

As for Temkin isotherm,

$$q_e = \frac{RT}{b} \ln K_T \, C_e \qquad \text{Eq. (2.3)}$$

Where,

b= heat of adsorption (J/mol.K)

K_T= Temkin constant (L/g)

2.6 Adsorption Kinetics

In the adsorption process, the adsorbent-adsorbate interactions could be determined when having a wide understanding of adsorption equilibrium and kinetics. Adsorption kinetics is used to understand the rate that governs the reaction and to determine the process's best conditions (Vieira *et al.*, 2020). Since BPA is one of the EDC, the main kinetic models used recently were pseudo-first-order and pseudo-second-order (Vieira *et al.*, 2020). These two models are essential in determining the mode of adsorption either physisorption or chemisorption.

2.6.1 Pseudo-First Order (PFO)

The pseudo-first-order model assumes that adsorption happens through a physisorption mechanism because film diffusion is the limiting stage. Non-linear PFO is applied to avoid any inaccurate estimation of parameters, k_1. For a long period, the PFO model was regarded as an empirical model (Wang and Guo, 2020b).

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad \text{Eq. (2.4)}$$

k_1= rate constant of pseudo-first-order (min^{-1})

2.6.2 Pseudo-Second Order (PSO)

The PSO model was utilised in most published literature to forecast adsorption experimental data and calculate adsorption rate constants. Similar to PFO, the non-linear equation is preferred due to inaccurate calculation and estimation of the parameter, k_2. The rate constant of PSO or k_2 is used to describe the rate of adsorption equilibrium (Wang and Guo, 2020b).

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad \text{Eq. (2.5)}$$

k_2= rate constant of pseudo-second order (g/mg min)

2.7 Adsorption Thermodynamics

To determine whether the adsorption process is either spontaneous or non-spontaneous, the analysis of thermodynamics study is important. According to Saha Papita and Shamik Chowdhurry, (2011) at a higher temperature, the adsorption process is more favorable in conjunction with the decrease in the negative value of Gibb's free energy. This is because the affinity of the adsorbate on the adsorbent increases as the temperature increases due to the increase of the mobility of adsorbate molecules at a high temperature. In contrast, if there is an increase in the negative value of Gibb's free energy indicates that the adsorption is more favorable at lower temperatures.

The Van't Hoff equation (Saha Papita and Shamik Chowdhurry, 2011) is used to study the parameter of thermodynamics in order to investigate BPA adsorption onto activated carbon at different temperature.

$$\Delta G^{\circ} = -RT \ln K_D \qquad \text{Eq. (2.6)}$$

Where,

$$K_D = \frac{C_a}{C_e} \qquad \text{Eq. (2.7)}$$

ΔG°= Gibb's free energy (KJ/mol)

R= Gas constant 8.314 J/mol.K

T= Temperature (K)

C_a = Equilibrium adsorbate concentration on adsorbent (mg/L)

C_e = Equilibrium adsorbate concentration in solution (mg/L)

When the process changes with temperature, equation above could be further integrated with respect to temperature,

$$\frac{d \ln K_D}{dT} = \frac{\Delta H^\circ}{RT^2}$$ Eq. (2.8)

Upon integration and rearrangement,

$$-RT \ln K_D = \Delta H^\circ - \gamma RT$$ Eq. (2.9)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$ Eq. (2.10)

Enthalpy and entropy can be obtained from the graph of ΔG° against temperature, T.

CHAPTER 3

MATERIALS AND METHODS

3.1 Material

The adsorbent used was the activated carbon (AC) from coconut shell, obtained from Thermodynamic Lab, School of Chemical Engineering, Universiti Sains Malaysia. On the other hand, Bisphenol A (BPA) was used as the adsorbate through this entire study. The properties of BPA are shown in the Table 3.1 below.

Table 3. 1 Chemical properties of BPA

Properties	**Description**
IUPAC Name	4,4'-Dihydroxy-2,2-Diphenylpropane
Common Name	Bisphenol A
Molecular Formula	$C_{15}H_{16}O_2$
Molecular Weight	228.29 g/mol
CAS Number	80-05-7
Boiling Point	220 °C
Melting Point	150.5 °C
Density	1.20 g/cm^3
Appearance	White to light brown flakes or powder
Solubility	<0.1 g/100 ml