POLYETHYLENEIMINE MODIFIED ACID TREATED SPENT TEA AS ADSORBENT FOR ASPIRIN REMOVAL

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ABSTRACT

Adsorption is a prominent process for the treatment of pharmaceutical compounds in wastewater which uses activated carbon (AC) as the adsorbent material. Unfortunately, due to high preparation cost in terms of chemical and energy usage, and poor tendency to be regenerated, the usage of AC at high scale is limited. Hence, there is a need to shift towards new substitutes that are both inexpensive and highly efficient, such as agricultural waste materials. To overcome the drawbacks of the AC, this study focuses on the synthesis of a new modified eco-friendly adsorbent using spent tea (discarded Camellia sinensis leaves). Other than safe and simple preparation method, it is also of low energy consumption since all the synthesis steps were done at low temperature and free of harmful materials and chemicals. Its application in the adsorption of aspirin from aqueous solution were conducted by batch adsorption technique. In this study, spent tea was modified with polyethyleneimine (PEI) via a crosslinking method with the usage of glutaraldehyde (GTA) as the crosslinker for the removal of aspirin. The spent tea initially underwent acid pre-treatment with the usage of phosphoric acid for washing and boosting the functional group purpose and afterwards called acid treated spent tea (TA). The best conditions to prepare PEI modified acid treated spent tea (TA-PEI) were 1 hour of acid pre-treatment, TA: PEI ratio of 1:2, and GTA concentration of 0.5%v/v. Afterwards, the TA-PEI was characterized using the Fourier transform infrared spectroscopy, Brunauer Emmett Teller area, CHNS Elemental analysis, scanning electron microscope analysis, and point of zero charge (pH_{pzc}). A batch experiment of adsorption studies was conducted and the results revealed a remarkable outcome with the adsorption capacity up to 88.9 mg/g under the following conditions: 30 minutes of contact time, pH 3, temperature of 30 °C, initial concentration of 200 mg/L and adsorbent dosage of 0.05 g. The experiment data were also fitted into kinetic, isotherm and thermodynamic models. The adsorption data fitted well with pseudo-second order model with the influence of intraparticle diffusion. For isotherm study, the data fitted well with Temkin model and the maximum capacity obtained was 150.8 mg/g. The thermodynamic studies proved that the adsorption of aspirin by TA-PEI is exothermic due to the negative enthalpy change value and it is spontaneous and feasible resulted from the negative value of Gibbs' free energy change. The regeneration study was conducted and it was revealed that TA-PEI has the tendency to be regenerated with the maximum cycle of 5. In a nutshell, TA-PEI adsorbent was successfully synthesised and revealed an outstanding adsorption performance. Hence, TA-PEI was proved as a new promising adsorbent for the removal of aspirin.

ABSTRAK

Penjerapan adalah proses yang penting untuk rawatan sebatian farmaseutikal dari air sisa yang menggunakan karbon teraktif (AC) sebagai bahan penjerap. Malangnya, disebabkan kos penyediaan yang tinggi hasil penggunaan kimia dan tenaga, selain dari kecenderungan yang rendah untuk digunapakai semula, penggunaan AC bagi skala besar adalah terbatas. Oleh yang demikian, terdapat keperluan untuk beralih kepada pengganti baharu yang bukan sahaja murah namun juga sangat berkesan, seperti bahan buangan dari pertanian. Untuk mengatasi kelemahan AC, kajian ini akan mengfokuskan kepada sintesis penjerap mesra alam terubahsuai baharu menggunakan sisa teh (daun Camellia sinensis). Selain kaedah penyediaan yang selamat dan mudah, ia juga rendah dalam penggunaan tenaga kerana proses sintesis menggunakan suhu yang rendah dan bebas dari bahan dan kimia yang berbahaya. Aplikasinya dalam penjerapan aspirin dari larutan akueus telah dijalankan menggunakan teknik penjerapan kelompok. Dalam kajian ini, sisa teh telah diubahsuai menggunakan polietilenaimina (PEI) melalui kaedah pemautsilangan dengan penggunaan glutaraldehida (GTA) sebagai pemautsilang bagi menyingkirkan aspirin. Pada mulanya, sisa teh telah melalui pra-rawatan asid menggunakan asid fosforik untuk tujuan pembasuhan dan penambahbaikan kumpulan dan seterusnya digelar sebagai sisa teh terawat asid (TA). Keadaan yang terbaik bagi penyediaan penjerap terubahsuai PEI dan terawat asid (TA-PEI) adalah 1 jam bagi masa pra-rawatan asid, nisbah antara TA: PEI adalah 1:2 dan kepekatan GTA sebanyak 0.5 %v/v. Seterusnya, penjerap TA-PEI telah dikaji ciri-cirinya menggunakan spektroskopi inframerah jelmaan Fourier, luas permukaan Brunauer Emmett Teller , titik cas sifar (pHpzc), dan analisis mikroskop elektron imbasan. Kajian penjerapan kelompok telah dijalankan dan hasil yang diperolehi sangat memuaskan dengan hampir 88.9 mg/g kapasiti penjerapan pada keadaan berikut; 30 minit masa sentuh, pH 3, suhu 30 °C, kepekatan awal 200 mg/L, dan dos penjerap 0.05 g. Maklumat penjerapan juga telah dimasukkan ke dalam pemodelan kinetik, isoterma, dan termodinamik. Model pseudo tertib kedua adalah yang paling sesuai dengan data penjerapan dengan pengaruh resapan antara zarah. Bagi kajian isoterma, maklumat penjerapan amat sesuai dengan model Temkin dan kapasiti maksimum yang diperolehi adalah 150.8 mg/g. Analisis termodinamik menunjukkan proses penjerapan aspirin oleh TA-PEI adalah bersifat eksotermik disebabkan nilai perubahan entalpi yang negatif, spontan dan boleh dilaksanakan kerana nilai perubahan tenaga bebas Gibb yang juga negatif. Kajian jana semula telah dijalankan dan didapati penjerap TA-PEI berjaya digunapakai semula sebanyak maksimum 5 kitaran. Kesimpulannya, penjerap TA-PEI telah berjaya disintensis dan menunjukkan prestasi yang cemerlang. Oleh itu, TA-PEI telah terbukti sebagai penjerap baharu yang menjanjikan penyinggiran aspirin.

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LIST OF ABBREVIATIONS

ha	-	Hectar
FAO		Food and Agriculture Organization of the United Nations
TA		Acid treated spent tea
TA-PEI	-	PEI modified acid treated spent tea
H_3PO_4	-	Phosphorus
NaOH	-	Sodium hydroxide
NSAIDs	-	Nonsteroidal Anti-Inflammatory Drugs
OFAT	-	One-Factor-at-A-Time
UV-Vis	-	Ultraviolet visible
GTA	-	Glutaraldehyde
PFO	-	Pseudo first order
PSO	-	Pseudo Second Order
WHO	-	World Health Organization
WWTP	-	Wastewaster Treatment Plant
pH_{pzc}	-	Point of zero charge
STP		Sewage treatment plant

LIST OF SYMBOLS

ΔH	-	Changes in enthalpy
ΔS	-	Changes in standard entrophy
ΔG	-	Gibbs free energy
mg/g	-	Milligram per gram
%	-	Percentage
°C	-	Degree celcius
mg/L	-	Milligram per litre
g	-	Gram
K_d	-	Dissociation coefficient
kJ/mol	-	Kilojoule per mole
mmol/g	-	Milimole per gram
min	-	Minute
R^2	-	Coefficient of determination
χ^2	-	Chi-squared
Hr	-	Hour

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The development in the health care sector investment, expand of the world population, advances in sciences and research, high pervasive of chronic diseases and the escalate of life expectancy increased the pharmaceutical compounds consumption over this past years (1). It is composed of diverse group of compounds designed to hindered and treat diseases (2). Non-steroidal anti-inflammatory drugs (NSAIDs) is among the common used types of drug which are beneficial to human health in pain relieving and soothing numerous inflammations such as rheumatic arthritis, osteoarthritis (3), pyretic and thrombosis (4). Aspirin also known as Acetyl Salicylic Acid (ASA) is one of the most common examples of the NSAIDs that is available over the counter and has been commonly used for pain relief of migraine, and prevention of first myocardial infarction, cardiovascular diseases, cancer, and treatment of human immuno-deficiency virus infection (3). These pharmaceutical compounds are classified as "emerging pollutants" and still being ignored of its severity and the importance of its proper disposal management. In Malaysia, even in the Environmental Quality Act 1974 (EQA) and other regulations (Malaysian legislation), the issue of pharmaceutical compounds are not getting a deserving attention and neither that it is properly addressed (5). Furthermore, there is no explicit regulation that governs the issue of pharmaceutical-safe source water where it is even considered as a non-priority pollutant (5–7).

Being extensively used in human and veterinary medicine, pharmaceutical compounds are now a major emerging environmental contaminants. Direct release into raw sewage, excretion by humans and animals, inadequate treatment in sewage treatment plants (STPs) and subsequent release into receiving waters are the normal routes of pharmaceutical compounds into the environment (1). These resulted in the continuous release of the pharmaceutical compounds in the environment and human health are threatened by the water consumption and usage especially as drinking water source (5). Treatment and removal of these wastes from the water is crucial in order to prevent the risks it may posed on the aquatic organisms. There are several advanced techniques that has been proposed by the researchers to tackle the issue of pharmaceutical waste contaminated water, such as, ion exchange method (8), membrane technology (9), wet oxidation method (10), and photocatalysis.

However, these are delicate processes and not always effective and economical wise (11). The non-volatile and non-biodegradable traits of pharmaceutical compounds allowing it to outflow the sedimentation and biological treatment in the STP resulted in the entrance of its metabolites in the water body (6). According to A & Lima (2018), these developed techniques has some shortage in terms of the convoluted procedures and maintenance, high investment cost, and toxic sludge and byproduct accumulation. Therefore, an effective alternative and treatment processes for the removal of aspirin from the water source is crucial and highly requisite. Among the procedures that evolved, adsorption is the one most reassuring and applicable for removing organic and inorganic micro pollutants (12). Álvarez-torrellas, Peres, Gil-álvarez, Ovejero, & García, (2017) and Bhatnagar & Anastopoulos (2017) claimed that adsorption poses numerous advantages. For instances, modest in terms of operation and design, handling micro level of pollutants ability, vigorous continuous and batch processes, toxicity removal, affordable investment cost, environmentally friendly, and high potential of adsorbent reuse and regeneration.

Activated carbon (AC) is a prominent compound in waste water treatment as it shows effective adsorption potential. Large surface area, highly developed porosity, and high extent of surface reactivity makes activated carbon an effective adsorbent material (11). Furthermore it poses excellent adsorption capacity and fast adsorption kinetics. These distinct traits make activated carbon a flexible material, which can eliminate various pollutants from numerous sources. Unfortunately, despite its high potential, the utilization of activated carbon is limited because it is costly (11,14). The synthesis of activated carbon usually involve the usage of various chemicals and high temperature for a long period of time for the activation and carbonization steps. For instance, bamboo AC undergo carbonization at 800°C for 1h then soaked in potassium hydroxide and dehydrated at 108°C overnight and finally pyrolysed for another 4h at high temperature up to 850°C (15). Hence, with the aim of going eco-friendly and low-cost simultaneously, attention has been shifted towards the materials which are byproduct of wastes from large scale industrial operations and agricultural waste as the source of adsorbent materials. Cheap and abundantly existing sources such as fly ash (16), cashew nutshell (17), pandan leaves (18), eggshell (19) and tea leaves (20,21) has the tendency to be used as commercial activated carbon substitutes (22).

This research will focus on the potential of using Spent Tea leaves or scientifically knows as *Camellia Sinensis* leaves as the adsorbent material as the spent tea are easily obtainable in daily life and of zero cost. The solid residue spent tea are obtained after the preparation of tea beverage by extraction with hot water which in the end will be discarded as a waste (23). According to Ying Pei et al., (2017), tea are being consumed over 18 billion cups daily and tea makers are having issues in disposing the used tea leaves after the tea extraction. Tea is one of the main products of the agricultural sector, with a high volume of waste, especially in the processing stage (24). The same situation are being observed here in Malaysia either in the restaurants or even at the household, where the abundantly available spent tea will only be disposed in the rubbish bin despite the facts that it can be reuse as a useful source. Tea is nominated to the second highest consumed beverage after water worldwide due to its refreshing and positive effects on health nature. As of just 2015, the global production of tea has doubled to 5305 million metric tons compared to 2525 million metric tons in 1995 (25). In India, the production of tea is estimated to reach 857,000 tonnes annually of which is the 27% of the total world production while the spent tea produced after the processing is approximately 190,400 tonnes (26). These number specifies the potential of the spent tea as a significant biomass source due to its abundance.

Apart from its availability, spent tea also fits the criteria as adsorbent; low-cost, abundant in nature, simple treating required and is a byproduct of waste materials (27). Furthermore, spent tea has the tendency to be utilised as adsorbent source as it is made up of 3.5-7.0% inorganic substances and high content of organic substances of 93.00-

96.50% (21). The insoluble cell walls of spent tea are highly composed of cellulose, hemicellulose, lignin, condensed tannins, and structural proteins thus it has the potential as an adsorbent (28). Moreover, the presence of hydroxyl, O-H group as the surface functional group in spent tea that came from the abundant polyphenols (29) compound in spent tea aid in its ability of adsorption (21).

However, despite the ability of spent tea as adsorbent, the adsorption capacity obtained are relatively low and could be improve with the means of treatments and surface modifications. As per said, appropriate modification on the biomass's surface has to be done to improve the adsorption ability and performance but without excessive utilization of energy and chemicals as in AC preparation (30). There are different modification process has previously been done by the researches on the waste-based adsorbents. For instances; the modified waste coffee with chitosan by solvent casting method (31), cationic surfactants modified coffee waste (32), hybrid chitosan-pandan (18), and base treated black tea waste (33).

In this study, surface modification were done on spent tea with the usage of Polyethyleneimine (PEI) as the surfactant and expected to yield high adsorption ability. PEI contains massive nitrogen-containing functional groups that will boost the adsorption performance (30). However, due to its high water solubility, PEI is unable to be use directly and require an insoluble solid support to act as an efficient hybrid adsorbent (34) . The abundant O-H groups in spent tea has a great tendency to react with the amine groups from PEI and led to the increase of active sites for adsorption to takes place (35). Hence, the impregnation of PEI and spent tea were expected to demonstrate excellent adsorption performance for pollutants from pharmaceutical wastewater such as aspirin.

1.2 Problem Statement

Being among the top prescribed pharmaceutical compounds in the world, aspirin usage and consumption is rated the highest among all pharmaceutical compounds in many countries including Malaysia (6,36). This can be attributed to the fact that aspirin is easily acquired as an over-the-counter medication mainly used to treat pain and fever. Proven by the previous research (6) done on the occurrence of pharmaceutical compounds in wastewater effluents and the surface water across rivers in Malaysia, high measure of aspirin were detected in all the sampling points hence demonstrated the extremely predominant of aspirin content in Malaysia water body. The stable and low biodegradation traits of aspirin resulted in the bioaccumulation of its molecules in the biological organisms which is also persistent in the environment. Severe effect of aspirin molecules on the physiological functions in biological systems as potential endocrine disrupters are worsened of the facts of human daily utilization of the contaminated water surface as the source of daily water usage especially for drinking water. Unfortunately, the loopholes in Malaysian legislation (5) on the proper disposal management of this pollutants added by the poor awareness on the severity of these pollutant subsequently posing threats on human health and aquatic system.

Adsorption is an eminent process for pharmaceuticals removal in wastewater due to its nifty and effective criteria such as low initial investment, operational simplicity, and environmental friendly. Activated carbon is well-known and commonly used in adsorption process and proven capable of eliminating few pharmaceuticals (1). Unfortunately, the usage of activated carbon are limited due to the high cost resulted from the poor tendency to be regenerated after adsorption and high production cost due to various chemicals usages and high heat energy to which then restricted its application in large scale (37). This leads to the interest in finding other substitutes that are cheaper, high adsorption capacity and are wastes-based.

Spent tea is an abundant household waste and even more easily available in a larger scale from tea processor plantation or any food and beverages outlets. Spent tea is an oxygen demanding pollutants and needs long period of biodegradation hence instead of ended up as environment pollutants, spent tea could be further investigate of its potential of being an adsorbent material. There are few research done on the potential of using spent tea for the treatment of waste water by adsorption. However, they are either as activated carbon, without any modification or with but of low unsatisfied capacity and the research on the adsorption of pharmaceutical waste, to be exact, aspirin are still scarce.

To provide the solution on the removal of aspirin in wastewater by adsorption and overcome the drawbacks of the activated carbon usage and low adsorption capacity of previously synthesis spent tea adsorbent as per mentioned, this research was done to investigated the tendency of using spent tea with surface modification done by a surfactant, PEI via crosslinking method on its adsorption of aspirin in aqueous solution. This is essential as up to date, there is still no research been done to determine the potential of using PEI modified spent tea for aspirin adsorption. Furthermore, this research could be one of the effort to solve the abundant issue of spent tea waste and to remove the pharmaceutical waste of aspirin. Moreover, during the synthesis stages and adsorption studies, the process were done mostly with the minimal chemical usage, low temperature of the reactions (room temperature to 90°C) since there is no activation or carbonization steps involved. This comply with the goals of producing the new alternative adsorbent of low cost, simple, environmental friendly and of waste-based sources.

1.3 Research Objectives

The objectives of the research are:

(a) To identify the best synthesis conditions of PEI modified spent tea, TA-PEI and its characteristic.

(b) To investigate adsorption performance of modified TA-PEI adsorbent on aspirin removal

(c) To study adsorbent kinetic, isotherm, and thermodynamic.

1.4 Research Scopes

The research study is subjected to several limitations. The scopes of this study consists of several parts including adsorbent preparation, characterization of adsorbent, adsorption study with several different variables, and also the kinetic, isotherm, and thermodynamic study of the sorbent. The following describes the limitations of the study in details

(a) The adsorbent of spent tea leaves were synthesised in two steps in which it will first undergo acid (phosphoric acid, H_3PO_4) treatment and subsequently modified with Polyethylenimine (PEI) via crosslinking method by using Glutaraldehyde (GTA) as the crosslinking agent. Effects of ratio of acid treated spent tea (TA) and PEI (1:1, 1:2,1:3, 2:1,3:1), and GTA concentration (0,0.5,1.0,2.0,3.0, and 4.0 v/v%) were investigated to identify the best conditions for the synthesis of TA-PEI. Then, adsorbents are subjected to FTIR and SEM studies for the observation of surface functional groups and topography and composition of the adsorbent. Specific surface area of the adsorbent will be determined using Brunauer-Emmett-Teller (BET). Few other characterizations were also done such as point of zero charge (pH_{pzc}) and CHNS elemental analysis.

(b) Adsorption studies were with several parameters being varied such as contact time (0 to equilibrium), initial pH solution (3-11), temperature (30-90°C), initial aspirin concentration (50-250mg/l), and adsorbent dosage (0.05-2.0 g) in order to obtain the best aspirin removal. Regeneration study were done on TA-PEI by simple washing process with distilled water throughout four cycles and the removal of aspirin were calculated for each cycle

(c) To analyse the adsorption kinetics of the aspirin, the pseudo-first-order, pseudo-second-order and intraparticle diffusion were applied. To analyse the adsorption isotherm of aspirin, the Langmuir, Freundlich, and Temkin were applied. The thermodynamics were evaluated by identifying the enthalphy change (ΔH), entropy change (ΔS), and Gibbs' free energy change (ΔG),.

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