MODIFICATION OF CARBON BLACK USING POLYETHYLENIMINE (PEI) FOR ASPIRIN REMOVAL

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Aspirin is the most common drug consumed by humans and animals, so there must be high demand on the production of this drug. Aspirin may bring adverse impact to humans and the environment even at low concentrations. This study was conducted to modify the carbon black by polyethylenimine (PEI) and characterize the modified carbon black (TC-PEI), to study the effect of various parameters during the adsorption process; as well as to analyse isotherm, kinetics, and thermodynamic behaviour of the adsorption. The carbon black obtained from the pyrolysis of tire waste provides an incentive to be used as a precursor to low-cost adsorbents due to its high carbon content. At first, the carbon black was treated by nitric acid to remove ash or sulphur content. Then, the impregnation of treated carbon black in PEI was done by varying the impregnation ratio, impregnation temperature and impregnation time. The best impregnation conditions are with one to two weight ratios of carbon black and PEI at 4 hours and 50°C. Next, the TC-PEI was used for adsorption studies. The TC-PEI was characterized in terms of surface morphology, surface area and functional group using field emission scanning electron microscopy, Brunauer-Emmett-Teller and Fourier transform infrared spectroscopy and point of zero charge, respectively. The kinetic, isotherm and thermodynamic studies were also performed. The adsorption process was seen fitted to the pseudo second-order and Langmuir isotherms. For thermodynamic studies, the adsorption gave an exothermic reaction, an increase in randomness and a spontaneous reaction. The regeneration study suggested two cycles for the adsorption of TC-PEI onto aspirin with 40% removal. From the results obtained, it gave the maximum capacity at 29.40 mg/g, which contributed to 60% aspirin removal within 120 minutes, at room temperature with pH 3 and 0.1 g of TC-PEI. In conclusion, the modified of TC by PEI can be used as an adsorbent for aspirin removal from pharmaceutical effluents.

ABSTRAK

Aspirin adalah ubat-ubatan yang paling biasa digunakan oleh manusia dan haiwan, oleh itu permintaan terhadap pengeluaran ubat ini sangat tinggi. Aspirin boleh membawa kesan yang buruk kepada manusia dan alam sekitar walaupun dalam kepekatan yang rendah. Kajian ini dijalankan untuk mengubahsuai karbon hitam dengan polietilinimina (PEI) dan menganalisa ciri-ciri karbon hitam terubahsuai (TC-PEI), untuk mengkaji kesan pelbagai parameter semasa proses penjerapan dan juga untuk menganalisa kelakuan isoterma, kinetik, dan kelakuan termodinamik penjerapan. Karbon hitam yang diperolehi dari pirolisis sisa tayar menyediakan insentif untuk digunakan sebagai prapenanda penyerap kos rendah kerana kandungan karbonnya yang tinggi. Pada mulanya, karbon hitam dirawat dengan asid nitrik untuk mengeluarkan kandungan abu atau sulfur. Kemudian, mengimpregnasi karbon hitam yang terawatt dalam PEI dilakukan dengan mengubah nisbah impregnasi, suhu impregnasi dan masa impregnasi. Keadaan impregnasi yang terbaik adalah dengan nisbah berat satu kepada dua oleh karbon hitam kepada PEI dalam tempoh 4 jam dan suhu 50°C. Seterusnya, TC-PEI digunakan untuk kajian penjerapan. Ciri-ciri TC-PEI telah dianalisa dari segi morfologi permukaan, luas permukaan dan kumpulan berfungsi dengan menggunakan mikroskop elektron imbasan pancaran medan, model Brunauer-Emmett-Teller dan spektroskopi inframerah jelmaan Fourier dan caj pada titik sifar. Kajian kinetik, isoterm dan termodinamik juga dilakukan. Proses penjerapan ini mengikut hukum pseudo tertib kedua dan isoterma Langmuir. Untuk kajian termodinamik, penjerapan memberikan tindakbalas eksotermik, peningkatan dalam rawak dan tindakbalas yang spontan. Kajian penjanaan semula mencadangkan bahawa dua kitaran untuk penjerapan TC-PEI terhadap aspirin dengan penyingkiran 40%. Dari hasil yang diperoleh, ia memberikan kapasiti maksimum pada 29.40 mg / g yang menyumbang 60% penyingkiran aspirin dalam keadaan 120 minit, pada suhu bilik dengan pH 3 dan 0.1 g TC-PEI. Sebagai kesimpulan, pengubahsuaian karbon hitam oleh PEI boleh digunakan sebagai penjerap untuk penyingkiran aspirin dari efluen farmaseutikal.

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LIST OF ABBREVIATIONS

PCPs	-	Pharmaceuticals and Personal Care Products
PEI	-	Polyethylenimine
CHNS	-	Carbon, hydrogen, nitrogen and sulphur
FTIR	-	Fourier Transform Infrared
BET	-	Brunauer-Emmett-Teller
FESEM	-	Field Emission Scanning Electron Microscopy
NSAIDs	-	Non steroid anti-inflammatory drug
STPs	-	Sewage treatment plant
MDL	-	Minimum detection limit
WWTP	-	Wastewater treatment plant
AC	-	Activated carbon
CNT	-	Carbon nanotube
CB	-	Carbon black
β-CD	-	β -cyclodextrin
D-R	-	Dubinin-Radushkevich
UV-Vis	-	Ultraviolet-visible
TC-PEI	-	Modified TC by PEI
TC	-	Treated carbon black
AC-STL	-	Activated carbon by spent tea leaves
AC-BCM	-	Activated carbon by babassu coconut mesocarp
P-AC	-	Activated carbon from Bologna-based Polichimica
SA-AC	-	Activated carbon from Sigma Aldrich
n/a	-	Not available

LIST OF SYMBOLS

ε	-	Polanyi potential
χ^2	-	Chi-squared error
R^2	-	Correlation coefficient
ΔH	-	Changes of enthalpy
ΔS	-	Changes of entropy
ΔG	-	Changes of Gibbs energy
°C	-	Celsius unit
C	-	Thickness of boundary layer
Ca	-	Calcium
Fe	-	Iron
L	-	litre
V	-	Volume of solution
m	-	Mass of adsorbent
R	-	Gas constant
T	-	Temperature
K	-	Kelvin unit
n	-	Heterogeneity of adsorption
g	-	gram
t	-	time
ng/L	-	Nano gram per litre
mL	-	Millilitre
mg/g	-	Milligram per gram
w/v	-	Weight per volume
C_f	-	Final concentration
C_o	-	Initial concentration
C_e	-	Equilibrium concentration
Q_t	-	Adsorption capacity at time
Q_e	-	Adsorption capacity at equilibrium
Q_m	-	Maximum adsorption capacity
Q_s	-	Saturation capacity

K_1	-	Rate constant for pseudo first-order
K_2	-	Rate constant for pseudo second order
K_d	-	Rate constant for intra particle diffusion
K_L	-	Langmuir constant
K_F	-	Freundlich constant
K_{ad}	-	D-R isotherm constant

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

In Malaysia, it was found that 3000 tonnes of waste were generated per day for 2013 and currently the waste generated reach 23 000 tonnes per day. The waste includes industrial waste, agricultural waste, pharmaceutical waste and domestic waste. A study by Ambali et al [1] reported that pharmaceutical waste in Malaysia is expected to reach 33 000 tons per year by 2020. Pharmaceutical compounds are biologically designed active to act through specific metabolic pathways.

Improper disposal or improper treatment of pharmaceutical waste might be hazardous which can contribute to the contamination of water supplies usually used by the communities or wildlife. Pharmaceuticals and Personal Care Products (PCPs) have been claimed as pollutant towards water or environment due to the indiscriminate disposal that poses a serious problem of ecological imbalance. One of the impacts of improper disposal or improper treatment of pharmaceutical waste is that it can kill or stop the growth of living cells along with extremely serious effects such as interference with reproductive processes in various life forms and antibiotic resistance.

Nowadays, the treatment and management of pharmaceutical waste have become a big challenge due to its hazardous nature [2]. Hence, the treatment of pharmaceutical compounds by conventional wastewater treatment method has become an issue due to ineffective removal of pharmaceuticals from wastewater. Adsorption has become the most efficient method as it is cost effective, simple to design and environmentally friendly. The most common adsorbent used for wastewater treatment is activated carbon due to its high effectiveness which can give high performance on pollutants removal. Besides, agricultural waste or industrial

waste are also widely used as a precursor for low-cost adsorbent, which are cheaper than the commercial activated carbon.

Many previous studies have mentioned that traditional or conventional wastewater treatment methods are not sufficient as the pharmaceutical waste cannot be completely removed [2]. Several advanced treatment methods that can be used to treat pharmaceutical waste include autoclaving, ion-exchange, advanced oxidation process and biological treatment. However, among these techniques, adsorption serves as a useful and efficient method to eliminate pharmaceutical waste due to its simple design and high effectiveness.

The increasing production of tire in industry contributed to the increasing amount of tire waste. The existence of tire waste in the country has increased environmental problems and health hazard. Disposing tire waste is a challenge as they are immune to biological degradation. Many studies have found that the pyrolysis of waste tire will produce valuable products, which are heating fuel and solid product [3]. The solid product comprises high content of carbon black that is suitable as an adsorbent. Hence, using carbon black as low-cost adsorbent will reduce the quantity of tire waste. In this study, the carbon black produced by the pyrolysis of tire waste was used as an adsorbent.

1.2 Problem Statement

The current commercialised adsorbent used to treat wastewater is activated carbon. Previous studies have mentioned that activated carbon is the most reliable and effective adsorbent. However, the usage of activated carbon is limited due to its high operating cost and high temperature applied for activation step. Thus, this study tries to explore adsorbent that is cheaper, easy to prepare as well as environmental-friendly.

Tire waste is highly abundant in Malaysia and can be one of the potential sources for low-cost adsorbent. The solid char produced by pyrolysis of tire waste

containing carbon black has a potential to be used as an activated carbon. There are many studies done on the uses of carbon black derived from tire waste as activated carbon. As mentioned earlier, activated carbon has its own drawback. Hence, this study explored the adsorption of pharmaceutical compounds using carbon black derived from tire waste without activation step. The carbon black was modified by polyethylinimine (PEI) to enhance the adsorption capacity because raw carbon black gives very bad performance in the removal of pollutants. PEI was used in this study as it is well-known as an effective surfactant in adsorption process. It is also one of the compounds that contain large number of amine groups. Therefore, it can be used to modify carbon black surface for the adsorption of pharmaceutical waste.

Pharmaceutical waste can cause harm to human health and environment. For this study, aspirin was focused due to its wide usage in the medical area. Aspirin is not totally mobilised in humans and animal body and this compound is excreted as a biologically active substance in wastewater [4]. The existence of this compound can affect the balance of ecosystem due to its accumulation which can contribute to the presence of antibiotic resistant microbial strains. Overdose of aspirin from industrial waste or other sources into the river or lake can cause harm to human being and aquatic life. The presence of this compound even at low concentration in the waste effluent could give physiological effects on animals and humans.

1.3 Objectives of Research

The objectives of the research are:

i. To modify carbon black by polyethylenimine (PEI) and characterize the modified carbon black for the adsorption of aspirin.

ii. To study the effect of various parameters during adsorption process which response to the removal of aspirin.

iii. To analyse isotherm, kinetics, and thermodynamics of the adsorption of aspirin onto modified carbon black.

1.4 Scope of Research

In order to achieve the objectives of the research, the scope of research was covered on the following aspect:

i. Raw carbon black produced from tire waste was treated by nitric acid to remove ash contents and then the treated carbon black was modified by chemical modification using polyethylinimine (PEI) with different ratios (1:1, 1:2, 2:1, 3:1, 1:3), different impregnation times (1, 2, 4, 6 and 24 hours) and different impregnation temperatures (30, 50 and 70°C). The characteristic of the modified carbon black was undergoing characterization of CHNS Elemental Analysis, FTIR, FESEM, BET and point of zero charge.

ii. The adsorption study was conducted by varying the parameter which are the effect of contact time (10-120 min), the effect of initial concentration (50-250 mg/L), the effect of solution pH (pH 3-pH 11), the effect of solution temperature (30°C-90°C) and the effect of adsorbent dosage (0.05-0.8 g) towards the removal of aspirin.

iii. The kinetic of reaction was analysed using pseudo first and pseudo second order kinetic model and intra-particle diffusion model. Moreover, to study the adsorption equilibrium, Langmuir, Freundlich and Dubinin-Radushkevich isotherm has been used. The adsorption thermodynamics was studied on the changes enthalpy (ΔH), changes in entropy (ΔS) and Gibbs energy (ΔG).

iv. Solvent regeneration method by distilled water was used in this study and the regeneration efficiency was calculated.

1.5 Significance of Research

This research was conducted to investigate the usage of carbon black as a precursor of adsorbent to treat pharmaceutical waste in order to reduce the environmental problem. This new alternative adsorbent can be prepared via simple procedure using mild condition yet capable with activated carbon. Hence, this research was using carbon black obtained from pyrolysis of tire waste and modified with PEI as an adsorbent. Utilization of carbon black as the activated carbon in adsorption process has been widely explored in previous studies to replace the expensive commercial activated carbon. There are only a few studies have been done on the use of carbon black as low-cost adsorbent without activation step and without modification process. Hence, this research is using carbon black derived from tire waste in order to replace the activated carbon. The carbon black was modified with PEI to enhance the adsorption capacity. This idea is one of the simplest design to synthesize the low-cost and environmental-friendly adsorbent. At the same time, this also can reduce the abundant amount of tire waste dumping in the country. Aspirin has been used as adsorbate in this research as a driving force which relate to the contamination of wastewater that affect the human health and aquatic life.

1.6 Thesis Outline

This thesis contains five chapters. For the Chapter 1, it is about research background, problem statement, research objectives, research scopes and significance of the research. Chapter 2 contains literature review on pharmaceutical compounds, adsorption process and adsorbent used for this research. In Chapter 3, it is about the methodology which includes the experimental setup, synthesis and characterization of modified carbon black and adsorption study. For the Chapter 4, it contains the results obtained and discussions. Some conclusions and recommendation are discussed in Chapter 5.

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