REMOVAL OF ASPIRIN AND PARACETAMOL FROM AQUEOUS SOLUTION BY USING TEA WASTE MODIFIED PEI ADSORBENT

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Specially thanks to

my family,

my friends,

and

to all that involve in this master project….

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ABSTRACT

The water bodies were determined to have been polluted by high concentration of pharmaceutical substances such as aspirin and paracetamol which may harm the ecosystem and bring health hazard to human. Conventional water treatment such as activated carbon used to remove these substances were not cost effective to be implemented. This study presented the alternative to the removal of aspirin and paracetamol from aqueous solution by using PEI modified tea waste adsorbent. The characteristics such as surface areas, pore volume and functional group of PEI-TW were identified by using Fourier Transform Infrared Spectroscopy (FTIR) and Brunauer-Emmett- Teller (BET). The total surface areas and pore volume of PEI-TW were 4.6748 m^2/g and 0.0249 cm^3/g, respectively. The highest removal percentage for aspirin was 87.34% in the optimum condition of initial concentration, dosage adsorbent; pH and temperature were 20 mg/L, 0.1g, pH 3 and temperature 60 ºC, respectively. Whereas removal of paracetamol achieved the percentage of 99.70% in the optimum condition of initial concentration, dosage adsorbent; pH and temperature were 20 mg/L, 0.1g, pH 7 and temperature 60 ºC, respectively. To describe the equilibrium isotherm for the adsorption of aspirin and paracetamol, the experimental data were fitted into Langmuir and Freundlich isotherm models, and both obeyed the Freundlich isotherm model with the correlation coefficient of 0.9865 and 0.9957 respectively. The adsorption process of aspirin and paracetamol obeyed the Pseudo-second order kinetic. The thermodynamic study indicated that the adsorption process of aspirin and paracetamol onto PEI modified tea waste adsorbent was feasible, spontaneous and endothermic. It can conclude that PEI modified tea waste adsorbent has high potential to be low-cost adsorbent and effective in the removal of paracetamol from aqueous solution compared to aspirin.

ABSTRAK

Sumber air didapati mempunyai kandungan farmaseutikal seperti aspirin dan paracetamol yang tinggi dimana ia boleh menganggu ekosistem dan memberi kesan kepada kesihatan manusia. Rawatan air konvensional seperti karbon diaktifkan yang berfungsi menyingkirkan bahan-bahan tersebut tidak begitu efektif dari segi kos. Kajian ini mencadangkan alternative dalam penyingkiran aspirin dan paracetamol dari larutan akueus menggunakan sisa teh yang dimodifikasi dengan polyethylenimine. Ciri-ciri seperti luas permukaan, isipadu dan kumpulan berfungsi di PEI-TW telah dikenal pasti dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR) dan Brunauer-Emmett Teller (BET). Jumlah luas permukaan dan isipadu PEI-TW adalah 4.6748 m^2/g dan 0.0249 cm^3/g. Penyingkiran aspirin yang tertinggi adalah 87.34% dan keadaan ini dicapai semasa dalam kondisi kepekatan awal 20 mg/L, dos penjerap 0.1g, pH 3 dan suhu 60 ºC. Manakala untuk penyingkiran paracetamol, peratus tertinggi yang diperolehi adalah 99.70% dengan kondisi kepekatan awal 20 mg/L, dos penjerap 0.1g, pH 7 dan suhu 60 ºC. Data eksperimen telah dianalisi dengan menggunakan model isotherm penjerapan: Langmuir dan Freundlich dan ia selaras dengan isoterma Freundlich yang memberikan koefisien korelasi sebanyak 0.9865 dan 0.9957 untuk penyingkiran aspirin dan paracetamol. Kadar penjerapan didapati mematuhi kinetik pseudo-tertib kedua. Kajian termodinamik menunjukkan bahawa penjerapan aspirin dan paracetamol boleh dilaksanakan, spontan dan endortermik. Dengan kesuluruhannya, keputusan menunjukkan bahawa PEI-TW boleh digunakan sebagai alternatif berkos rendah untuk penyingkiran paracetamol daripada larutan akueus jika dibandingkan dengan penyingkiran aspirin.

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LIST OF ABBREVIATIONS

AB45	-	Acid Blue 45
AO8	-	Acid Orange 8
APAP	-	Paracetamol
ARGs	-	Antibiotic Resistance Genes
ASA	-	Aspirin
BET	-	Brunauer-Emmett-Teller
C	-	Carbon
$C_8H_8O_4$	-	Aspirin
$C_8H_9NO_2$	-	Paracetamol
CBZ	-	Carbamazepine
CPC	-	Cetylpyridium Chloride
CR	-	Congo Red
CTAB	-	Cetyltrimethyl Ammonium Bromide
Cu	-	Copper
Fe/N-CNT/β-CD	-	Iron and Nitrogen Base Nanocomposite Polymer
Fe_3O_4 NPs	-	Magnetite Nanoparticles
FTIR	-	Fourier Transform Infra-Red
H	-	Hydrogen
HCL	-	Hydrochloric Acid
IUPAC	-	International Union of Pure and Applied Chemistry
KNO_3	-	Potassium Nitrate
MGEs	-	Mobile Genetic Elements
N	-	Nitrogen
NaOH	-	Sodium Hydroxide

NaOH	-	Sodium Hydroxide
N-CNT/β-CD	-	Nitrogen Base Nanocomposite Polymer
$NO+SO_2$	-	Pyrolysed Waste Tea Char
O	-	Oxygen
OH	-	Hydroxyl Group
PACs	-	Pharmaceutically Active Compounds
Pb	-	Lead
PCA	-	Paracetamol
PEI	-	Polyethylenimine
PEI-TW	-	Tea Waste Modified using PEI
SMX	-	Sulfamethoxazole
TMP	-	Trimethoprim
TW	-	Tea Waste
UV	-	Ultra Violet
$ZnCl_2$	-	Zinc Chloride

LIST OF SYMBOLS

Ce	-	Equilibrium concentration
Cm^3/g	-	Centimeter cubed per gram
Co	-	Initial concentration
g	-	Gram
g/L	-	Gram per litre
g/mol	-	Gram per mol
hr (s)	-	Hour (s)
µg/L	-	Microgram per litre
µm	-	Micro Meter
g/mol	-	Gram/mole
g/cm^3	-	Gram per cubic centimetre
J	-	Joule
K	-	Kelvin
kJ	-	Kilo Joule
k1	-	Adsorption rate constant of first order adsorption
k2	-	Adsorption rate constant of second order adsorption
K_F	-	Freundlich constant
kJ/mol	-	Kilo Joule per mol
K_L	-	Langmuir constants related to the rate of adsorption
kp	-	Intraparticle diffusion rate constant
kV	-	Kilovolt
L	-	Liter
M	-	Molar
m^2/g	-	Meter square per gram

mg	-	Milligram
mg/g	-	Milligram per gram
mL	-	Mililitre
mg/L	-	Milligram per litre
min	-	Minute
mm	-	Milimetre
ng/L	-	Nanograms/litre
nm	-	Nanometre
q_e	-	Amount of adsorbed on adsorbent at equilibrium
q_m	-	Maximum adsorption capacity
q_t	-	Amount of adsorbed on adsorbent at any time
R	-	Universal gas constant
R^2	-	Regression Coefficient
R_L	-	Separation factor
% w/v	-	weight/volume percent
ΔG^o	-	Gibbs energy changes
ΔH^o	-	Enthalpy change
ΔS^o	-	Entropy change
^oC	-	Degree celcius
%	-	Percentage
<	-	Less than
>	-	Greater than

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Water pollution is a major environmental concern that is caused by pollutants that are discharged to water stream from sources with inadequate water treatments. Industrial wastewater is apparently one of the main sources that released these harmful compounds, also known as pollutants. There are many types of pollutants that originate from industrial wastewater effluents and one of them is antibiotics. Antibiotics are extensively utilised in different type of industries, especially in pharmaceutical and personal care products. Up to 100 μg L^{-1} of various pharmaceuticals were found in aqueous environment, soil and mostly in effluents from drug manufactures (Fakhri and Behrouz, 2015). The high concentration of antibiotics existing in industrial water is a troubling issue as it can cause several health effects to human and aquatic life.

Large amount of antibiotics such as antibiotic resistance genes (ARGs) and mobile genetic elements (MGEs) are harbour from pharmaceutical waste. It can increase the prevalence of single- and multiple-antibiotic resistance among Acinetobacter species in wastewater treatment plant, which may affect the efficiency of antibiotic removal by anaerobic digestion (Liu *et al.*, 2014). These antibiotics present in water bodies are considered toxic and harmful as it can cause several health effects to human and aquatic life due to it assisting pathogen to be antibiotic-immune, making it hard to remove or destroy the pathogen (Romero, 2012).

Various low-cost materials especially natural or wasted materials have been extensively explored for adsorption removal of antibiotics from aqueous solution. Commonly used natural raw materials such as coal, wood, pit shells, coconut and nut shells are used to manufacture absorbents. One of the commonly known natural waste is tea waste. The large consumption of tea is found in Turkey, which is the world's largest black tea producing country (Gondogdu *et al.*, 2013). It leads to a significant amounts of tea waste being generated. Therefore, an efficient utilization of tea wastes has been gaining considerable attention and absorbent produce from tea waste will be used to remove antibiotics in industrial wastewater.

For improving the affinity of a material to pharmaceutical substances, various cationic surface modifications have been explored and studied. Polyethylenimine (PEI) is a relatively cheap cationic polymer that can be used for surface modification of an adsorbent. It has been proven in previous researches that it has the capability to enhance the removal of other anionic pollutant such as anionic metals and dyes (Deng and Ting, 2005; Won *et al.*, 2011). This polymer can readily bind with anionic substrate. Therefore, with the surface modification of tea waste, adsorption of pharmaceutical substances using tea waste can be widely implemented in industries in the future to remove various classes of pharmaceutical substances from wastewater.

1.2 Problem Statement

The presence of paracetamol and aspirin in water bodies could bring adverse effect to the human health and the environment, even in a low concentration (<0.1 mg/L). It could disrupt the biological function of micro-organism in wastewater treatment plant, reducing its efficiency in removal, furthermore promoting resistance development to the pathogen, which were harmful to human health (Larsson *et al.*, 2014).

Adsorption method was considered as the most effective wastewater treatments process to reduce the hazardous material in the wastewater. Nowadays, the adsorbent that was widely employed for adsorption in industry was commercial activated carbon. However, its production method was limited and costly due to the usage of strong acidic activating agent. Therefore, it was vital that an alternative material which was cost-effective as well as abundant to be used as the adsorbent for substances removal from wastewater (Yagub *et al.*, 2014).

Tea waste which was regarded as an inexpensive and abundant, obtainable at the amount of 30 000 tons from the extraction process of instant tea manufacturing (Malkoc and Nuhoglu, 2006) and the final residues originated from cafeteria which could act as a promising adsorbent for antibiotic removal (Gundogdu *et al.*, 2013). It has been proven that plant based materials appeared to be the best raw material and were suitable for large-scale production as they are abundant (Sebastian, 2017). Hence, the removal efficiency of antibiotics for tea waste adsorbent can be enhanced through a surface modification on the tea waste. Polyethylenimine (PEI) was a cationic polymer that was proved to be exemplary in its surface modification role for the removal of anionic pollutant such as anionic metals and dyes (Deng and Ting, 2005; Low et al., 2008, Won *et al.,* 2011; Sadaf *et al.*, 2014). This was due to the significant amount of positively charged amine groups from PEI introduced to the surface of adsorbent in which it could readily bind to anionic substrate. Thus, tea waste impregnated with PEI could be used as a potential adsorbent for antibiotic removal from aqueous solution.

1.3 Objectives

The objectives of this research are:

i) To synthesize and characterize PEI-modified tea waste as the adsorbent for paracetamol and aspirin removal.

ii) To investigate the effect of the physicochemical parameters such as pH, temperature, contact time, initial paracetamol and aspirin concentration and adsorbent dosage on paracetamol and aspirin adsorption performance of PEI-modified tea waste.

iii) To analyse the adsorption behaviour of PEI-modified tea waste using isotherm, kinetic, and thermodynamic analysis.

1.4 Research Scope

Paracetamol and aspirin for this study will be prepared in a solution and the adsorbent used were from natural waste material which was known to be inexpensive and abundant. In addition to that, the type of material used to modify the surface of the adsorbent was a cationic polymer. Moreover, the characterization of the adsorbent was conducted using analytical instrumentation, which was Fourier Transform Infrared (FTIR) Spectrophotometer and Brunauer-Emmett-Teller (BET).

Furthermore, this study was done under various parameters which were pH, temperature, contact time, initial substances concentration and adsorbent dosage. The range of the solution pH that the adsorption study was carried out is in the range of pH 2 to pH 9. As for operational temperature, the adsorption study was conducted in the range of 30^{o}C to 60^{o}C. For initial paracetamol and aspirin concentration, the adsorption process was conducted with initial concentration between 0.02 g/L to 0.1 g/L. Also, the adsorbent dosage that will be used in this study were in the range of 0.1 to 1.0 g. For the equilibrium study, the Langmuir and Freundlich isotherms were applied. The Pseudo first-order, Pseudo second-order and intraparticle diffusion were applied for the kinetic study. The thermodynamics parameters of the adsorption of the adsorption of acetaminophen including the Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) were calculated by using Van't Hoff equation.

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