REMOVAL OF ASPIRIN FROM AQUEOUS SOLUTION USING PHOSPHORIC ACID -MODIFIED COFFEE WASTE ADSORBENT

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Specially dedicated to

my parents
my brother
my sisters,
and my best friends

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ABSTRACT

Removal of pharmaceutical waste, aspirin (ASA) in aqueous solution was investigated using activated carbon derived from coffee waste(CW). Activated carbon was prepared by using phosphoric acid as a chemical activating agent. Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the functional groups on the surface of the adsorbents. The surface area of the adsorbent was measured by BET technique. The activated carbon derived from coffee waste modified by H_3PO_4 was observed to have a larger surface area than AC-CW. The states of the adsorption operations are controlled by the effect of initial ASA concentration, adsorbent dose, contact time, temperature and pH adjacent on the adsorption procedure. In the batch adsorption test, the highest removal efficiency found was 98.02% in 30 minutes and 95% in 60 minutes when used H_3PO_4 - AC-CW and AC-CW respectively. The optimum conditions for removal of aspirin from aqueous solution was found to be at 1000 mg/L of initial concentration ASA , pH 4 and at a temperature of 30°C and 0.5 g of H_3PO_4 - AC-CW and 0.6g AC-CW adsorbents. The experimental data for adsorption of aspirin were well fitted into Langmuir isotherm model and obeyed pseudo-second order kinetics model. The adsorption of aspirin onto H_3PO_4- AC-CW and AC-CW were exothermic in nature, with enthalpy change $\Delta H° = - 0.182$ kJ/mol and -0.216 kJ/mol, $\Delta S°$ was 0.072 J/mol -0.004 J/mol , which indicates a decrease in randomness at the adsorbent surface/aspirin solution interface, respectively. A negative Gibbs free energy $\Delta G°$ was obtained indicating feasibility and spontaneity of the adsorption process. For this study, the coffee waste modified by H_3PO_4 modified is considered as promising adsorbent and it could be employed as a low cost alternative to commercial activated in removal of aspirin in aqueous solutions.

ABSTRAK

Penyingkiran bahan buangan farmaseutikal, aspirin (ASA) dalam larutan akueus telah dikaji dengan menggunakan karbon diaktikan daripada sisa kopi (CW). Karbon diaktifkan disintesis dengan menggunakan asid fosforik sebagai agen pengaktif kimia. Fourier Transform Infrared Spectroscopy (FTIR) digunakan untuk mencirikan kumpulan berfungsi di permukaan penjerap. Luas permukaan dan morfologi penjerap diukur menggunakan teknik BET. Karbon diaktifkan daripada sisa kopi dengan menggunakan H_3PO_4 dilihat mempunyai luas permukaan yang lebih besar berbanding AC-CW. Kondisi penjerapan diperolehi dengan mengawal faktor-faktor yang mempengaruhi proses jerapan seperti kepekatan ASA, dos penjerap, masa, suhu dan pH. Ujian penjerapan secara kelompok mendapati penyingkiran yang tertinggi ialah 98.02 %pada 30 minit dan 95 % pada 60 minit untuk penjerap H_3PO_4 - AC-CW dan AC-CW. Kondisi optima untuk penyingkiran aspirin dalam larutan akueus ialah 1000 mg/L kepekatan ASA, pH 4, suhu pada 30 °C dan 0.5 g dos bagi H_3PO_4 - AC-CW penjerap and 0.6 g dos bagi AC-CW penjerap,. Penilaian untuk data jerapan ASA telah menunjukkan mematuhi dengan baik bagi teori model isoterm Langmuir dan kinetik pseudo-second order. Penjerapan ASA oleh H_3PO_4 - AC-CW dan AC-CW adalah bersifat eksotermik, dengan perubahan entalpi masing-masing ialah $\Delta H°$ = -0.182 kJ/mol dan -0.216 kJ/mol, $\Delta S°$ ialah 0.072 - 0.004 J/mol, nilai ini menunjukkan penurunan secara rawak pada permukaan penjerap/aspirin. Nilai negative oleh tenaga bebas Gibbs $\Delta G°$ yang diperolehi menunjukkan proses jerapan boleh dilaksanakan dan berlaku secara spontan. Berdasarkan hasil daripada kajian ini, sisa kopi yang diubahsuai menggunakan H_3PO_4 dianggap sebagai penjerap yang efektif dan ia boleh digunakan sebagai alternatif kos rendah bagi komersial karbon yang diaktifkan untuk penyingkiran aspirin di dalam larutan akueus.

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LIST OF ABBREVIATIONS

AC	-	Activated Carbon
ASA	-	Aspirin(acetylsalicylic acid)
BET	-	Brunauer-Emmett-Teller
CW	-	Coffee waste
FTIR	-	Fourier Transform Infra-Red
H_2O	-	Water
H_3PO_4	-	Phosphoric Acid
HCl	-	Hydrochloric Acid
NaOH	-	Sodum Hydroxide
N_2	-	Nitrogen Gas
NaOH	-	Sodium Hydroxide
NaCl	-	Sodium Chloride
PHW	-	Pharmaceutical Waste
UV	-	Ultra Violet

LIST OF SYMBOLS

C_e	-	Equilibrium concentration
C_0	-	Initial concentration
g	-	Gram
g/mol	-	Gram per mol
hr (s)	-	Hour (s)
μm	-	Micro Meter
J	-	Joule
K	-	Kelvin
K_{eq}	-	Equilibrium constant
k_1	-	Adsorption rate constant of first order adsorption
k_2	-	Adsorption rate constant of second order adsorption
K_F	-	Freundlich constant
kg	-	Kilogram
kJ	-	Kilo Joule
kJ/mol	-	Kilo Joule per mol
K_L	-	Langmuir constants related to the rate of adsorption
L	-	Liter
M	-	Molar
m^2/g	-	Meter square per gram
mg	-	Milligram
mg/g	-	Milligram per gram
mg/L	-	Milligram per liter
min	-	Minute
K_F	-	Freundlich constant
°C	-	Degree celcius

q_e	-	Amount of adsorbent at equilibrium
q_t	-	Equilibrium rate constant
q_{max}	-	Maximum adsorption capacity
R^2	-	Correlation coefficient
T	-	Absolute solution temperature
t	-	Time
V	-	Volume
W	-	Weight of adsorbent
wt%	-	Weight percent
$\Delta G°$	-	Gibbs Free Energy
$\Delta H°$	-	Entropy
$\Delta S°$	-	Entropy

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water contamination by pharmaceutical wastes has caused significant environmental issues since the mid-1990s. Over a decade, researchers have detected low concentrations of pharmaceutically active compounds (PHAC) in surface water , groundwater and drinking water (Doerr-MacEwen, 2007). The current information from Canada demonstrates that the most consumed drugs are acetylsalicylic acid (Aspirin), acetaminophen (Paracetamol), ibuprofen, naproxen carbamazepine and antimicrobial operators. Pharmaceutical waste have brought huge worries due to their potential risk to the nature and human health, and this potential issue is not to be disparaged (Doerr-MacEwen, 2007).

The manufacture of pharmaceutical products has expanded rapidly within few decades. This subsequently leads to the increase in the release of pharmaceutical wastes to the water bodies. Conventional wastewater treatments for pharmaceutical waste contaminants have found to be ineffective as well as insufficient in reducing a large portion of these compounds. Therefore, lingering amounts remain in the treated water, and have been found to accumulate in drinking water (Ferreira *et al.*, 2015). So, the focus of this study will be based on one sort of pharmaceutical waste, namely: Aspirin (ASA) which has negative effects on human health and the environment.

There are numerous approaches to expel pharmaceutical waste from sewage. However, some of them are costly. Lately, little efforts have been employed in the utilization of coffee waste (CW) as an adsorbent. In view of past understanding, it was found that coffee is one of the primary product in world trade value. Reusing coffee waste has environmental and economic importance (Nowicki *et al.*, 2014). Coffee industry produces a lot of waste in all phases of coffee production,starting from harvesting to the finished product. Coffee has been studied and found to have a high adsorption capacity, because of its properties. The polar nature of coffee waste can remove huge amounts of metal ions from aqueous solutions (Al-Zaben and Mekhamer, 2013). In addition to that, coffee waste fundamentally contains weak acidic and basic functional groups (Kyzas, 2012).

The adsorption of Aspirin will be conducted by using coffee waste . CW is used in two ways, one of which is the use of raw CW without the addition of any chemicals and another way is using of CW modified with Phosphoric Acid (H_3PO_4). Using these wastes as raw materials for pharmaceutical waste treatment will give more sustainable solution that will also reduce them from landfills (Mayanga-Torres *et al.*, 2017). Aspirin is considered weak acids that are positively charged. The surface charge of the modified CW can be altered to a negative charge. Therefore, the surface of modified CW could be a promising adsorbent to remove the positive charged pharmaceutical waste from the water bodies. The two methods will be compared whichever is more efficient in terms of removal of Aspirin.

1.2 Problem Statement

Nowadays, up to thousands of tonnes per year of medicines for human are being produced and consumed(Tapia-Orozco et al., 2016), this has leads to improper disposal of pharmaceutical wastes into the environment (water bodies). According to a report associated with US (*"pharmaceuticals and contaminated packaging were discarded by hospitals and long-term care facilities estimated 250 million pounds"*) (Donn *et al.*, 2009). The event and extent of pharmaceuticals in water resources have been reported in two relatively recent analyses carried out in the US, which reviewed the natural risk participatory in exposing therapeutic substances to the environment (Kolpin et al., 2002). The negative effects of these therapeutic substances include cancer (Moreira *et al.*, 2016) . Hence ,it is imposed to treat the pharmaceutical waste before being released to the environment. Water contamination often occurs due animal wastes and human activities that tend to discharge wastes to water bodies. Therefore, pharmaceutical waste enter to our water indirectly. In this study, Aspirin is chosen since it is the world's most consumed type of drug for relieving pain. On the other and Aspirin is said to many side effects to human being because it can result in headache, nausea and even harmful impacts on the liver and kidney.

There are many ways to remove pharmaceutical wastes from wastewater. These include advanced technologies such as Ozonation, Advanced Oxidation processes, reverse osmosis activated carbon and membrane filtration. Moreover, the widely used thermal regeneration activated carbon is costly and in addition, it is indirect causes of the environmental problem (Anastopoulos *et al.*, 2017; Ferreira *et al.*, 2015). Therefore, using an alternative low-cost adsorbent, that does not represent an economic cornerstone for the large-scale implementation of these water treatments processes, is of paramount importance. Moreover, the use of largely available residues, as precursors of low-cost carbon adsorbents, to remove pharmaceutical wastes by effective technique (Mestre *et al.*, 2011) is more sustainable.

The coffee residue is an inexpensive substance that is readily available around the world where the coffee is produced according to the International Coffee Organization, "*coffee production amounted to around 680 million tonnes*" (Reffas et al., 2010). The coffee residues can be used to remove cationic pharmaceutical waste from waste water. This is due to the fact that CW surface can be activated using H_3PO_4 as an activating agent to convert the charge on its surface from positive to negative charge. The resulting used H_3PO_4 is non-contaminating substance, it can be disposed by leaching with water and also it can be reused after water washing. Moreover, phosphoric acid is normally used for the preparation of carbon adsorbents with microporous surface (Reffas et al., 2010). Furthermore, activated carbon from plant species are said to have high specific surface area and they are obtained in the temperature range of (450–500) °C (Reffas et al., 2010).

1.3 Objectives

The objectives of this research are:

i. To prepare and characterize H_3PO_4-modified coffee waste as the adsorbent for Aspirin removal.

ii. To investigate the effect of the physicochemical parameters such as pH, temperature, contact time, initial Aspirin concentration and adsorbent dosage on the Aspirin adsorption performance of H_3PO_4-modified coffee waste.

iii. To study the adsorption behaviour of H_3PO_4-modified coffee waste using isotherm, kinetic, and thermodynamic analysis.

1.4 Scope of Study

Aspirin is chosen for this study ,which is sort of cationic pharmaceutical waste and the adsorbent proposed to be used are from the characteristic waste material of CW, which is known to be economical and copious. Moreover, the characterization of the adsorbent is conducted using analytical instrumentation such as Fourier Transform Infrared (FTIR) Spectrophotometer and Brunauer-Emmett-Teller (BET) analysis. The adsorption behaviour of the adsorbents considered for this research is utilising adsorption isotherm and dynamic models, as well as thermodynamic investigation. Furthermore, this study is done under various parameters which are :

i. Contact time, the experiments were conducted for 210 minutes.
ii. The range of the solution pH that the adsorption study was carried out was in the range of pH (2- 11).
iii. For operating temperature, the adsorption study was conducted in the range of (30-50) °C.
iv. For initial Aspirin concentration, the adsorption process is conducted with initial Aspirin concentration (1000 – 5000) mg/L.
v. The adsorbent dosage that was used in this study was in the range of 0.1 to 0.6 g.

1.5 Research Significance

Pharmaceutical products are generally used on humans and animals for treatment and prevention of diseases by affecting their physiological and biochemical processes. Some medicines are used as antibiotics, pain relievers and infections. There are many improper disposal methods such as metabolic processes produced by human and animal which cause contamination of water sources in the long term.

Choosing an absorbent material will be environmental friendly, an inexpensive cost and is readily available. Coffee waste has been chosen as it is known to be a good absorbent for Aspirin from aqueous solution. Coffee waste surface will be modified by phosphoric acid to make it negatively charged for adsorption of ASA ,which has a positive charge and a weak acid. CW could be more efficient than other materials used as adsorbent materials for remove ASA .

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