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

REHAM SALAH HASSAN BOUSHARA

A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

FEBRUARY 2018

Specially dedicated to

my parents
my brother
my sisters,
and my best friends

ACKNOWLEDGEMENT

I would like to thank Thank you Almighty God for his blessings upon me that I managed to complete this research work. I would also like to express my sincere thanks to my Dr. Norzita bint Ngadi who guided me and helpe me in all all steps to make sure I complete the work successfully

My heartfelt appreciation to UTM for providing students with all the required facilities for their research in terms of research sites and the availability of materials and tools to carry out research, I am very proud that I graduated from this university and be one of its students.

The most beautiful words of thanksgiving and gratitude to the most cherished people in my life for what they have given me. I hope that God gives you health and wellness because you deserve all the best. If I could offer you my age as a kind of gratitude, I would not late to give you a moment. To those who sacrificed for me a lot and gave up their happiness for my comfort and happiness. They taught me a lot of values and principles, who stood by my side in my intensity and prosperity, the least I can offer you is the recognition of your gratitude, thank you, love people to my heart- my mother, my father, my brother, my sisters. May God prolong your lives.

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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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^3	-	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

LIST OF APPENDICES

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 .

REFERENCES

Abdeen, Z., and Mohammad, S. G. (2013). Study of the adsorption efficiency of an eco-friendly carbohydrate polymer for contaminated aqueous solution by organophosphorus pesticide. *Open Journal of Organic Polymer Materials, 2014.*

Abdel-Shafy, H. I., and Mohamed-Mansour, M. S. (2013). Issue of Pharmaceutical Compounds in Water and Wastewater: Sources, Impact and Elimination. *Egyptian Journal of Chemistry, 56*(5), 449-471.

Agarwal, A. K., Kadu, M. S., Pandhurnekar, C. P., and Muthreja, I. L. (2014). Langmuir, Freundlich and BET Adsorption Isotherm Studies for Zinc ions onto coal fly ash. *Int. J. Appl. Innov. Eng. Manage.(IJAIEM), 3*(1), 64-71.

Ahmadi, M., Motlagh, H. R., Jaafarzadeh, N., Mostoufi, A., Saeedi, R., Barzegar, G., et al. (2017). Enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater using MWCNT/TiO 2 nano-composite. *Journal of Environmental Management, 186*, 55-63.

Al-Odaini, N. A., Zakaria, M. P., Zali, M. A., Juahir, H., Yaziz, M. I., and Surif, S. (2012). Application of chemometrics in understanding the spatial distribution of human pharmaceuticals in surface water. *Environmental monitoring and assessment, 184*(11), 6735-6748.

Al-Zaben, M., and Mekhamer, W. (2013). Removal of 4-chloro-2-methyl phenoxy acetic acid pesticide using coffee wastes from aqueous solution. *Arabian Journal of Chemistry.*

Ali, S. A., Al Hamouz, O. C. S., and Hassan, N. M. (2013). Novel cross-linked polymers having pH-responsive amino acid residues for the removal of Cu 2+ from aqueous solution at low concentrations. *Journal of hazardous materials, 248*, 47-58.

ALOthman, Z. A. (2012). A review: fundamental aspects of silicate mesoporous materials. *Materials, 5*(12), 2874-2902.

Anastopoulos, I., Karamesouti, M., Mitropoulos, A. C., and Kyzas, G. Z. (2017). A review for coffee adsorbents. *Journal of Molecular Liquids, 229*, 555-565.

Ayar, A., Gürsal, S., Gürten, A. A., and Gezici, O. (2008). On the removal of some phenolic compounds from aqueous solutions by using a sporopollenin-based ligand-exchange fixed bed—Isotherm analysis. *Desalination, 219*(1-3), 160-170.

Ballesteros, L. F., Ramirez, M. J., Orrego, C. E., Teixeira, J. A., and Mussatto, S. I. (2017). Optimization of autohydrolysis conditions to extract antioxidant phenolic compounds from spent coffee grounds. *Journal of Food Engineering, 199*, 1-8.

Ballesteros, L. F., Teixeira, J. A., and Mussatto, S. I. (2014). Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. *Food and bioprocess technology, 7*(12), 3493-3503.

Beijer, K., Björlenius, B., Shaik, S., Lindberg, R. H., Brunström, B., and Brandt, I. (2017). Removal of pharmaceuticals and unspecified contaminants in sewage treatment effluents by activated carbon filtration and ozonation: Evaluation using biomarker responses and chemical analysis. *Chemosphere, 176*, 342-351.

Brunauer, S., Emmett, P. H., and Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American chemical society, 60*(2), 309-319.

Chapman, P. M., Ho, K. T., Munns, W. R., Solomon, K., and Weinstein, M. P. (2002). Issues in sediment toxicity and ecological risk assessment. *Marine pollution bulletin, 44*(4), 271-278.

Coyle, C., Cafferty, F. H., Rowley, S., MacKenzie, M., Berkman, L., Gupta, S., et al. (2016). ADD-ASPIRIN: A phase III, double-blind, placebo controlled, randomised trial assessing the effects of aspirin on disease recurrence and survival after primary therapy in common non-metastatic solid tumours. *Contemporary Clinical Trials, 51*, 56-64.

Crittenden, J. C., Howe, K. J., Hand, D. W., Tchobanoglous, G., and Trussell, R. R. (2012). *Principles of Water Treatment*: John Wiley & Sons, Incorporated.

Cryer, B., and Feldman, M. (1998). Cyclooxygenase-1 and cyclooxygenase-2 selectivity of widely used nonsteroidal anti-inflammatory drugs. *The American journal of medicine, 104*(5), 413-421.

Dai, Y., Zhang, D., and Zhang, K. (2016). Nitrobenzene-adsorption capacity of NaOH-modified spent coffee ground from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers, 68*, 232-238.

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L., and Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *water research, 46*(6), 1947-1957.

Deiminiat, B., Razavipanah, I., Rounaghi, G. H., and Arbab-Zavar, M. H. (2017). A novel electrochemical imprinted sensor for acetylsalicylic acid based on polypyrrole, sol-gel and SiO 2@ Au core-shell nanoparticles. *Sensors and Actuators B: Chemical, 244*, 785-795.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: a review. *Journal of hazardous materials, 157*(2), 220-229.

Doerr-MacEwen, N. A. (2007). The management of human pharmaceuticals in the environment.

Donn, J., Mendoza, M., and Pritchard, J. (2009). AP IMPACT: Tons of released drugs taint US water. *ABC News (April 19, 2009), available at http://abcnews. go. com/Technology/wireStory.*

Donohue, M., and Aranovich, G. (1998). Classification of Gibbs adsorption isotherms. *Advances in colloid and interface science, 76*, 137-152.

Elmouwahidi, A., Bailón-García, E., Pérez-Cadenas, A. F., Maldonado-Hódar, F. J., and Carrasco-Marín, F. (2017). Activated carbons from KOH and H 3 PO 4-activation of olive residues and its application as supercapacitor electrodes. *Electrochimica Acta, 229*, 219-228.

Ferreira, R., Couto Junior, O., Carvalho, K., Arroyo, P., and Barros, M. (2015). Effect of solution pH on the removal of paracetamol by activated carbon of dende coconut mesocarp. *Chemical and Biochemical Engineering Quarterly, 29*(1), 47-53.

Foo, P., and Lee, L. (2010). *Preparation of activated carbon from Parkia Speciosa Pod by chemical activation.* Paper presented at the Proceedings of the World Congress on Engineering and Computer Science.

Freundlich, H. (1909). *Kapillarchemie, eine Darstellung der Chemie der Kolloide und verwandter Gebiete, von Dr. Herbert Freundlich*: akademische Verlagsgesellschaft.

Ganiyu, S. O., van Hullebusch, E. D., Cretin, M., Esposito, G., and Oturan, M. A. (2015). Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: a critical review. *Separation and Purification Technology, 156*, 891-914.

Gros, M., Petrović, M., Ginebreda, A., and Barceló, D. (2010). Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. *Environment international, 36*(1), 15-26.

Gulipalli, C. S., Prasad, B., and Wasewar, K. L. (2011). Batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA). *J. Eng. Sci. Technol, 6*(5), 586-605.

Hansson, L., Zanchetti, A., Carruthers, S. G., Dahlöf, B., Elmfeldt, D., Julius, S., et al. (1998). Effects of intensive blood-pressure lowering and low-dose aspirin in patients with hypertension: principal results of the Hypertension Optimal Treatment (HOT) randomised trial. *The Lancet, 351*(9118), 1755-1762.

He, L., Sun, X., Zhu, F., Ren, S., and Wang, S. (2017). OH-initiated transformation and hydrolysis of aspirin in AOPs system: DFT and experimental studies. *Science of The Total Environment, 592*, 33-40.

Heberer, T. (2002). Tracking persistent pharmaceutical residues from municipal sewage to drinking water. *Journal of Hydrology, 266*(3), 175-189.

Ho, Y.-S. (2006). Review of second-order models for adsorption systems. *Journal of hazardous materials, 136*(3), 681-689.

Hao, Y.-f., Yan, L.-g., Yu, H.-q., Yang, K., Yu, S.-j., Shan, R.-r., et al. (2014). Comparative study on adsorption of basic and acid dyes by hydroxy-aluminum pillared bentonite. Journal of Molecular Liquids, 199, 202-207.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: a review. Carbohydrate polymers, 45(3), 253-267.

Húmpola, P., Odetti, H., Fertitta, A., and Vicente, J. (2013). Thermodynamic analysis of adsorption models of phenol in liquid phase on different activated carbons. *Journal of the Chilean Chemical Society, 58*(1), 1541-1544.

Ismail, M. G. B. H., Weng, C. N., Rahman, H. A., and Zakaria, N. A. (2013). Freundlich Isotherm Equilibrium Equastions in Determining Effectiveness a Low Cost Absorbent to Heavy Metal Removal In Wastewater (Leachate) At Teluk Kitang Landfill, Pengkalan Chepa, Kelantan, Malaysia. *Journal of Geography and Earth Science, 1*(1), 01-08.

Jeon, C. (2017). Adsorption and Recovery of Immobilized Coffee Ground Beads for Silver Ions from Industrial Wastewater. *Journal of Industrial and Engineering Chemistry.*

Jung, K.-W., Choi, B. H., Hwang, M.-J., Jeong, T.-U., and Ahn, K.-H. (2016). Fabrication of granular activated carbons derived from spent coffee grounds by entrapment in calcium alginate beads for adsorption of acid orange 7 and methylene blue. *Bioresource Technology, 219*, 185-195.

Kårelid, V., Larsson, G., and Björlenius, B. (2017). Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. *Journal of Environmental Management, 193*, 491-502.

Kumar, A., and Jena, H. M. (2016). Preparation and characterization of high surface area activated carbon from Fox nut (Euryale ferox) shell by chemical activation with H 3 PO 4. *Results in Physics, 6*, 651-658.

Kyzas, G. Z. (2012). Commercial coffee wastes as materials for adsorption of heavy metals from aqueous solutions. *Materials, 5*(10), 1826-1840.

Lafi, R., and Hafiane, A. (2016). Removal of methyl orange (MO) from aqueous solution using cationic surfactants modified coffee waste (MCWs). *Journal of the Taiwan Institute of Chemical Engineers, 58*, 424-433.

Langmuir, I. (1916). THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. PART I. SOLIDS. *Journal of the American Chemical Society, 38*(11), 2221-2295.

Li, X., Strezov, V., and Kan, T. (2014). Energy recovery potential analysis of spent coffee grounds pyrolysis products. Journal of Analytical and Applied Pyrolysis, 110, 79-87.

Lide, D. R. (2007). CRC Handbook of chemistry and physics. B&T: Oxford.(Online accessed: www. hbcpnetbase. com, last visited: 24.08. 2008).

Lima, E. C., Royer, B., Vaghetti, J. C., Simon, N. M., da Cunha, B. M., Pavan, F. A., et al. (2008). Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution: kinetics and equilibrium study. *Journal of hazardous materials, 155*(3), 536-550.

Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthes, V., and Krimissa, M. (2007). Sorption isotherms: a review on physical bases, modeling and measurement. *Applied Geochemistry, 22*(2), 249-275.

Liu, Y., and Liu, Y.-J. (2008). Biosorption isotherms, kinetics and thermodynamics. *Separation and Purification Technology, 61*(3), 229-242.

Lua, A. C., Yang, T., and Guo, J. (2004). Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. *Journal of analytical and applied pyrolysis, 72*(2), 279-287.

Madikizela, L. M., Tavengwa, N. T., and Chimuka, L. (2017). Status of pharmaceuticals in African water bodies: Occurrence, removal and analytical methods. *Journal of Environmental Management, 193*, 211-220.

Mayanga-Torres, P., Lachos-Perez, D., Rezende, C., Prado, J., Ma, Z., Tompsett, G., et al. (2017). Valorization of coffee industry residues by subcritical water hydrolysis: Recovery of sugars and phenolic compounds. *The Journal of Supercritical Fluids, 120*, 75-85.

Meade, E. A., Smith, W. L., and Dewitt, D. L. (1993). Differential inhibition of prostaglandin endoperoxide synthase (cyclooxygenase) isozymes by aspirin and other non-steroidal anti-inflammatory drugs. *Journal of Biological Chemistry, 268*(9), 6610-6614.

Meischl, F., Schemeth, D., Harder, M., Köpfle, N., Tessadri, R., and Rainer, M. (2016). Synthesis and evaluation of a novel molecularly imprinted polymer for the selective isolation of acetylsalicylic acid from aqueous solutions. *Journal of Environmental Chemical Engineering, 4*(4), 4083-4090.

Mestre, A. S., Bexiga, A. S., Proença, M., Andrade, M., Pinto, M. L., Matos, I., et al. (2011). Activated carbons from sisal waste by chemical activation with K 2 CO 3: kinetics of paracetamol and ibuprofen removal from aqueous solution. *Bioresource technology, 102*(17), 8253-8260.

Moreira, F. C., Soler, J., Alpendurada, M., Boaventura, R. A., Brillas, E., and Vilar, V. J. (2016). Tertiary treatment of a municipal wastewater toward pharmaceuticals removal by chemical and electrochemical advanced oxidation processes. *Water Research, 105*, 251-263.

Moussavi, G., Momeninejad, H., Shekoohiyan, S., and Baratpour, P. (2017). Oxidation of acetaminophen in the contaminated water using UVC/S 2 O 8 2− process in a cylindrical photoreactor: Efficiency and kinetics of degradation and mineralization. *Separation and Purification Technology, 181*, 132-138.

Mphahlele, K., Onyango, M. S., and Mhlanga, S. D. (2015). Adsorption of aspirin and paracetamol from aqueous solution using Fe/N-CNT/β-cyclodextrin nanocomopsites synthesized via a benign microwave assisted method. Journal of Environmental Chemical Engineering, 3(4), 2619-2630.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., and Takada, H. (2006). Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water research, 40*(17), 3297-3303.

Nasuha, N., Hameed, B. & Din, A. T. M. 2010. Rejected Tea as a Potential Low-Cost Adsorbent for the Removal of Methylene Blue. Journal of Hazardous Materials 175(1): 126-132.

Neibi, M. C. (2008). Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis. *Journal of Hazardous Materials, 153*(1), 207-212.

Neil, M. J. (2006). The Merck Index: An Encyclopedia of chemicals, drugs and biologicals. Whitehouse station, New Jersey: Published by Merck Research Laboratories, Division of Merck and Co: Inc.

Nicolaou, K., Magolda, R., Smith, J. B., Aharony, D., Smith, E., and Lefer, A. (1979). Synthesis and biological properties of pinane-thromboxane A2, a selective inhibitor of coronary artery constriction, platelet aggregation, and thromboxane formation. *Proceedings of the National Academy of Sciences, 76*(6), 2566-2570.

Nowicki, P., Skibiszewska, P., and Pietrzak, R. (2014). Hydrogen sulphide removal on carbonaceous adsorbents prepared from coffee industry waste materials. *Chemical Engineering Journal, 248*, 208-215.

Pei, J., Yao, H., Wang, H., Ren, J., and Yu, X. (2016). Comparison of ozone and thermal hydrolysis combined with anaerobic digestion for municipal and pharmaceutical waste sludge with tetracycline resistance genes. *Water research, 99*, 122-128.

Peters, T. (2010). Membrane technology for water treatment. *Chemical engineering & technology, 33*(8), 1233-1240.

Pujol, D., Liu, C., Gominho, J., Olivella, M., Fiol, N., Villaescusa, I., et al. (2013). The chemical composition of exhausted coffee waste. Industrial Crops and Products, 50, 423-429.

Reffas, A., Bernardet, V., David, B., Reinert, L., Lehocine, M. B., Dubois, M., et al. (2010). Carbons prepared from coffee grounds by H 3 PO 4 activation: characterization and adsorption of methylene blue and Nylosan Red N-2RBL. *Journal of hazardous materials, 175*(1), 779-788.

Ribeiro, A. B., Mateus, E. P., and Couto, N. (2015). *Electrokinetics Across Disciplines and Continents: New Strategies for Sustainable Development*: Springer.

Rowlands, G. J. (2001). Experimental Organic Chemistry Daniel R. Palleros. John Wiley & Sons: New York. 2000. 833 pp. $86.95. ISBN 0-471-28250-2: ACS Publications.

Ruiz, B., Cabrita, I., Mestre, A. S., Parra, J. B., Pires, J., Carvalho, A. P., et al. (2010). Surface heterogeneity effects of activated carbons on the kinetics of paracetamol removal from aqueous solution. *Applied Surface Science, 256*(17), 5171-5175.

Sacchetti, M. (2014). Thermodynamics of water–solid interactions in crystalline and amorphous pharmaceutical materials. *Journal of pharmaceutical sciences, 103*(9), 2772-2783.

Schmidt, A. (1943). *Die industrielle Chemie in ihrer Bedeutung im Weltbild*: Verlag Walter de Gruyter.

Shashidhar, M., Giridhar, P., and Manohar, B. (2017). Kinetics and thermodynamics in downstream processing of medicinal fungi C. sinensis CS1197. *Biochemical Engineering Journal, 121*, 88-93.

Shen, K., and Gondal, M. (2013). Removal of hazardous Rhodamine dye from water by adsorption onto exhausted coffee ground. *Journal of Saudi Chemical Society*.

Sing, K. S. 1985. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). Pure and applied chemistry 57(4): 603-619.

Sumathi, T. & Alagumuthu, G. 2014. Adsorption Studies for Arsenic Removal Using Activated Moringa Oleifera. International Journal of Chemical Engineering 2014(

Tang, Y., and Singh, J. (2008). Controlled delivery of aspirin: effect of aspirin on polymer degradation and in vitro release from PLGA based phase sensitive systems. *International journal of pharmaceutics, 357*(1), 119-125.

Tapia-Orozco, N., Ibarra-Cabrera, R., Tecante, A., Gimeno, M., Parra, R., and Garcia-Arrazola, R. (2016). Removal strategies for endocrine disrupting chemicals using cellulose-based materials as adsorbents: A review. *Journal of Environmental Chemical Engineering, 4*(3), 3122-3142.

Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., et al. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry, 87(9-10), 1051-1069.

Wang, N., Jin, R.-N., Omer, A., and Ouyang, X.-k. (2017). Adsorption of Pb (II) from fish sauce using carboxylated cellulose nanocrystal: Isotherm, kinetics, and thermodynamic studies. *International Journal of Biological Macromolecules, 102*, 232-240.

Wols, B., Hofman-Caris, C., Harmsen, D., and Beerendonk, E. (2013). Degradation of 40 selected pharmaceuticals by UV/H 2 O 2. *Water research, 47*(15), 5876-5888.

Wong, S., Lee, Y., Ngadi, N., Inuwa, I. M., and Mohamed, N. B. (2017). Synthesis of activated carbon from spent tea leaves for aspirin removal. *Chinese Journal of Chemical Engineering.*

Yorgun, S., and Yıldız, D. (2015). Preparation and characterization of activated carbons from Paulownia wood by chemical activation with H 3 PO 4. *Journal of the Taiwan Institute of Chemical Engineers, 53*, 122-131.

Yuh-Shan, H. 2004. Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions. Scientometrics 59(1): 171-177.