ADSORPTION OF NICKEL IONS FROM AQUEOUS SOLUTION BY EXHAUSTED COFFEE GROUNDS

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For my beloved family and best of friends.
For the love, motivation and patience.
Thank you.

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ABSTRACT

The possible use of exhausted coffee grounds as an adsorbent for the removal of nickel (II) ions from aqueous solution was investigated as a potential low-cost an alternative treatment to treat wastewater containing nickel (II) and other heavy metal ions. The effects of relevant parameters including contact time, initial concentration and particle size on nickel(II) adsorption were examined. This experiment was conducted at room temperature and no pH adjustment was made prior to the analysis. Batch adsorption studies also revealed that the amount of nickel (II) ions adsorbed per gram weight of exhausted coffee grounds increased with an increased in initial Ni (II) ions concentration with 75.10 to 98.17% of nickel ions removed. The effect of particle size of the exhausted coffee grounds varied for different initial nickel(II) ions concentration studied. Kinetic studies and adsorption isotherm were performed to investigate the mechanism of adsorption of nickel (II) ions. Adsorption data indicated that the adsorption of nickel(II) ions by exhausted coffee grounds was best described by pseudo-second-order kinetic model and Freundlich isotherm model. The exhausted coffee ground from Arabica origin with particle size of 420 - 212µm exhibited a better adsorption than other origin and particle size with a percentage of 96.00 to 98.00% of nickel(II) ions removal for all initial ion concentration tested.

ABSTRAK

Penggunaan sisa kopi sebagai bahan penjerap untuk menyingkirkan ion nikel(II) dari larutan akues telah dikaji sebagai salah satu bahan penjerap berpotensi yang murah dan merupakan alternatif untuk rawatan sisa air yang mengandungi ion nikel(II) serta lain-lain ion logam berat. Penjerapan ion nikel (II) telah dijalankan dengan mempelbagaikan pembolehubah seperti masa olakan, kepekatan awal logam nikel (II) dan saiz partikel sisa kopi. Kajian ini telah dijalankan pada suhu bilik dan sebarang pelarasan pH tidak dijalankan sebelum analisis. Kajian penjerapan berkelompok juga menunjukkan bahawa jumlah ion nikel(II) yang dijerap per gram jisim sisa kopi meningkat sejajar dengan peningkatan kepekatan awal ion nikel (II) dengan 75.10 hingga 98.17% ion nikel(II) disingkirkan. Kesan saiz partikel sisa kopi terhadap penjerapan ion nikel(II) oleh sisa kopi adalah berubah-ubah mengikut kepekatan awal ion nikel(II) yang dikaji. Kajian kinetik dan isoterma penjerapan juga telah dijalankan untuk mengkaji mekanisma penjerapan ion nikel(II). Data penjerapan menunjukkan bahawa penjerapan ion nikel(II) oleh sisa kopi adalah sesuai dengan model kinetik pseudo-tertib-kedua dan model isoterma Freundlich. Sisa kopi dari jenis Arabica dengan saiz 420 - 212µm menunjukkan penjerapan yang lebih baik berbanding jenis dan saiz partikel yang lain, dengan peratusan penyingkiran ion nikel(II) sebanyak 96.00 hingga 98.00% untuk semua kepekatan awal ion yang dikaji.

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LIST OF ABBREVIATIONS

R^2	-	Correlation Coefficient
Ni	-	Nickel
As	-	Arsenic
Cd	-	Cadmium
Cr	-	Chromium
Cu	-	Copper
Pb	-	Lead
Zn	-	Zinc
mg l^{-1}	-	milligram per liter
PAC	-	powdered activated carbon
GAC	-	granular activated carbon
K	-	Kelvin
mg	-	milligram
SEM	-	Scanning Electron Microscope
EDTA	-	Ethylenediaminetetraacetic acid
nm	-	nanometer
µm	-	micrometer
mm	-	millimeter
g	-	gram
l	-	liter
ppm	-	part per million
ml	-	milliliter
g l^{-1}	-	gram per liter
min	-	minute

UV-Vis	-	Ultraviolet-Visible
mg g^{-1}	-	milligram per gram
PAN	-	1-(2 Pyridylazo)-2-Naphtol

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CHAPTER 1

INTRODUCTION

1.1 Introduction

One of the major sources of aquatic pollution is industrial wastewater. Heavy metals are one of the pollutants that have gained significance due to their persistence, bio-magnification and toxicity (Tolani *et al.*, 2009; Kadirvelu *et al.*, 2001; Khan *et al.*, 2004). The release of toxic heavy metals to water streams has been seriously contributed by rapid industrialization. Sources of heavy metal contamination include mining, electroplating, metal processing, textile and battery manufacturing (Amarasinghe and Williams, 2007; Kadirvelu *et al.*, 2001). Restrictive regulations of allowable level of heavy metals discharge have been introduced and practiced in many countries in order to minimize the impact to the environment (Tolani *et al.*, 2009) and later have accelerated the developments of highly efficient technologies for heavy metal removal.

Recently, the removal of heavy metals such as nickel, lead and zinc from contaminated waters has become a major topic of research, due to the toxicological effects on environment and human health. The conventional methods of removal used are ion-exchange, reverse osmosis, electrodialysis, dilution, adsorption, filtration, precipitation, flotation, air-stripping, steam stripping and chelation (Nityanandi *et al.*, 2006; Sud *et al.*, 2008; Tolani *et al.*, 2009). However, current treatment processes proposed by most researchers and scientists are expensive and not suitable to be used in most developing countries due to economic factor (Bailey *et al.*, 1999; Utomo and Hunter, 2007). Though adsorption could provide a cost

effective solution among other method of removal, some adsorbents are yet expensive. Therefore, natural waste materials from various industrial processes have been re-used for additional purposes in removing heavy metal, rather than simple disposal. Due to environmental and commercial sense, researchers and scientists have focused on the used of agricultural and food industry wastes such as coffee grounds, tea and rice hull (Low *et al.*, 2000; Oliveira *et al.*, 2008). Tannin-containing materials such as coffee grounds are believed to be good low-cost adsorbents for dissolved heavy metals (Utomo and Hunter, 2007).

Coffee has become an established beverage in many parts of the world including Europe, America and Asia (Tokimoto *et al.*, 2005). Significant amount of waste is generated by coffee processing industries. Most of these grounds are burned as waste, dumped in landfill, as animal feed or boiler fuel (Tokimoto *et al.*, 2005; Utomo and Hunter, 2007). Development of researches to reuse coffee grounds for useful purpose would definitely help to convert this waste into a new resource. Part of the development is using exhausted coffee grounds as alternative adsorbent to remove hazardous pollutant from wastewater (Adachi *et al.*, 2008; Khenniche and Aissani, 2009; Oliveira *et al.*, 2007; Tan, 1985; Utomo and Hunter, 2007).

This study, however, focus on the removal of nickel ion from aqueous solution using various types of exhausted coffee grounds. Batch study was conducted and the Langmuir and Freundlinch isotherm models were tested for the adsorption of nickel by exhausted coffee grounds.

1.2 Problem Statement

Adsorption with activated carbon has attracted the eyes of many researchers because of the effectiveness for the removal of heavy metal ion at trace quantities. However, it has not been used extensively for its high cost. For that reason, the use of low cost adsorbents as alternative for metal removal from wastewater has been highlighted. Great effort has been contributed to develop and improve existing

adsorbents. The use of agricultural waste is one of the exploitation, due to its high availability and no need of complicated regeneration processes. Exhausted coffee grounds were used in this research as adsorbent for nickel ions. However, its effectiveness is unknown and needs to be determined.

1.3 Objectives

The objective of the study is to propose an alternative use for exhausted coffee grounds, as adsorbents for the removal of nickel ions from aqueous solutions. The specific objectives are can be categorized as follows:

i. To investigate the effect of contact time, initial ion concentration, and effect of different types and sizes of exhausted coffee grounds for the removal of Ni(II) ion from aqueous solution;
ii. To determine the adsorption kinetics and adsorption isotherms for the removal of Ni(II) ions from aqueous solution

1.4 Scopes of the Study

i. Three different types of exhausted coffee grounds were used in this study. The grounds were the result from the steam extraction to produce instant coffee and were collected from various locations in Malaysia. No chemical treatment was performed on the grounds prior to the adsorption experiments.
ii. The concentration of nickel (Ni(II)) ion was measured using HACH DR/5000 Spectrophotometer.
iii. The effect of contact time and initial Ni(II) ion concentration, percentage of Ni(II) ion removal from aqueous solution, effect of particle size of the exhausted coffee grounds were studied.

iv. The Lagergren pseudo-first-order and pseudo-second order models were used to study the kinetic of the adsorption for the Ni(II) ion removal.

v. Adsorption isotherm was investigated using Langmuir and Freundlich isotherm models.

1.5 Significance of the Study

The findings will be used in further research and the exhausted coffee grounds can be used as an alternatively low-cost adsorbent in heavy metal removal especially in removing nickel from aqueous solution. The knowledge obtained from this research will allow the selection of the more efficient, effective and economic treatment for industrial wastewaters using adsorption method.

REFERENCES

Abbasi, S. A., Abbasi, N.and Soni, R. (1998). *Heavy Metals in the Environment,* New Delhi, Mittal Publication.

Adachi, A., Ioku, A., Taniyama, K.and Okano, T. (2008). Use of Tea or Coffee Lees as Adsorbent for Removal of Benzene from Wastewater. *Journal of Health Science,* **54,** 478 - 481.

Adams, M. R.and Dougan, J. (1987). Waste Products. *In:* Clarke, R. J.andMacrae, R. (eds.) *Cofee Volume 2: Technology.* London: Elsevier Applied Science Publisher Ltd.

Adi, A. J.and Noor, Z. M. (2009). Waste Recycling: Utilization of Coffee Grounds and Kitchen Waste in Vermicomposting. *Bioresource Technology,* **100,** 1027 - 1030.

Agarwal, S. K. (2009). *Heavy Metal Pollution,* New Delhi, APH Publishing Corporation.

Ahmadpoura, A., Tahmasbi, M., Bastami, T. R.and Besharati, J. A. (2009). Rapid Removal of Cobalt Ion from Aqueous Solutions by Almond Green Hull. *Journal of Hazardous Materials* **166,** 925–930.

Aklil, A., Mouflih, M.and Sebti, S. (2004). Removal of Heavy Metal Ions from Water by Using Calcined Phosphate as a New Adsorbent. *Journal of Hazardous Materials,* **A112** 183–190.

Amarasinghe, B. M. W. P. K.and Williams, R. A. (2007). Tea Waste as a Low Cost Adsorbent for the Removal of Cu and Pb from Wastewater. *Chemical Engineering Journal* **132,** 299–309.

Aziz, H. A., Adlan, M. N.and Ariffin, K. S. (2008). Heavy Metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) Removal from Water in Malaysia: Post Treatment by High Quality Limestone. *Bioresource Technology,* **99,** 1578-1583.

Bailey, S. E., Olin, T. J.and Bricka, R. (1999). A Review of Potentially Low-Cost Sorbents for Heavy Metals. *Water Resources,* **33,** 2469-2479.

Bansal, M., Garg, U., Singh, D.and V.K.Garg (2009a). Removal of Cr(VI) from Aqueous Solutions using Pre-Consumer Processing Agricultural Waste: A Case Study of Rice Husk. *Journal of Hazardous Materials,* **162,** 312–320.

Bansal, M., Singh, D., V.K.Gargand Rose, P. (2009b). Use of Agricultural Waste for the Removal of Nickel Ions from Aqueous Solutions: Equilibrium and Kinetics Studies. *International Journal of Civil and Environmental Engineering* **1,** 108 - 114.

Bhatnagar, A., Minocha, A. K.and Sillanpää, M. (2010). Adsorptive Removal of Cobalt from Aqueous Solution by Utilizing Lemon Peel as Biosorbent. *Biochemical Engineering Journal,* **48,** 181 - 186.

Bhatnagar, A.and Sillanpää, M. (2010). Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment—A Review. *Chemical Engineering Journal* **157** 277–296.

Bhattacharya, A. K., Mandal, S. N.and Dasa, S. K. (2006). Adsorption of Zn(II) from Aqueous Solution by Using Different Adsorbents. *Chemical Engineering Journal* **123** 43–51.

Birge, W. J.and Black, J. A. (1980). Aquatic Toxicology of Nickel. *In:* Nriagu, J. O. (ed.) *Nickel in The Environment.* Canada: John Wiley & Sons.

Curcovic, L. C.-S.and Rastovean-Mioe, A. (2001). Batch Pb^{2+} and Cu^{2+} Removal by Electric Furnace Slag. *Water Resources,* **35,** 3436 - 3440.

Demirbas, A. (2004). Adsorption of Lead and Cadmium Ions in Aqueous Solutions onto Modified Lignin from Alkali Glycerol Delignication *Journal of Hazardous Materials,* **B109,** 221 - 226.

Demirbas, E., Kobya, M.and Konukman, A. E. S. (2007). Error Analysis of Equilibrium Studies for the Almond Shell Activated Carbon of Cr(VI) from Aqueous Solution. *Journal of Hazardous Materials,* **154,** 787 - 794.

Demirbas, E., Kobya, M., Oncel, S.and Sencan, S. (2002). Removal of Ni(II) from Aqueous Solution by Adsorption onto Hazelnut Shell Activated Carbon: Equilibrium Studies. *Bioresource Technology,* **84,** 291 - 293.

Din, A. T. M., Hameed, B. H.and Ahmad, A. L. (2009). Batch adsorption of phenol onto physiochemical-activated coconut shell. *Journal of Hazardous Materials,* **161,** 1522–1529.

Duffus, J. H. (2002). "Heavy Metals" - A Meaningless Term? (IUPAC Technical Report). *Pure Appl. Chem.*: International Union Pure and Applied Chemistry

Hadjmohammadi, M. R., Salary, M.and Biparva, P. (2011). Removal of Cr(IV) from Aqueous Solution Using Pine Needles Powder as a Biosorbent. *Journal of Applied Sciences in Environmental Sanitation,* **6,** 1 - 13.

Halstead, T. (2010). *Coffee: World Markets and Trade. June 2010*. United States Department of Agriculture. Available: http://www.fas.usda.gov/htp/coffee/2010/June 2010/2010_June_Coffee.pdf [Accessed April 16 2011].

Hameed, B. H. (2009). Spent Tea Leaves: A New Non-Conventional and Low-cost Adsorbent for Removal of Basic Dye from Aqueous Solutions. *Journal of Hazardous Materials* **161** 753–759.

Hameed, B. H.and Daud, F. B. M. (2007). Adsorption Studies of Basic Dye on Activated Carbon Derived from Agricultural Waste: *Hevea brasiliensis* Seed Coat. *Chemical Engineering Journal* **139,** 48–55.

Hassanien, M. A.and Shahawy, A. M. E. Year. Environmental Heavy Metals and Mental Disorders of Children in Developing Countries. *In:* Simeonov, L. I., Kochubovski, M. V.and Simeonova, B. G., eds. NATO Advanced Research Workshop on Environmental Heavy Metal Pollution and Effects on Child Mental Development - Risk Assessment and Prevention Strategies, (2010) Sofia, Bulgaria. Springer.

Ho, Y. S. (2006). Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods *Water Research,* **40,** 119 - 125.

Ho, Y. S.and Mckay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry* **34** 451–465.

Huang, C. P.and Blankenship, D. W. (1984). The Removal of Mercury (II) from Dilute Aqueous Solution by Activated Carbon. *Water Resources,* **18,** 37-46.

I. N. S. G. 2010. World Nickel Statistic: Monthly Bulletin April (2010). *In:* Consumption, G. N. P. A. (ed.) *http://www.insg.org/stats.aspx*. Lisbon

Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N.and Pattabhi, S. (2003). Utilization of Various Agricultural Wastes for Activated Carbon Preparation and Application for the Removal of Dyes and Metal Ions from Aqueous Solutions. *Bioresource Technology,* **87,** 129-132.

Kadirvelu, K., Thamaraiselvi, K.and Namasivayam, C. (2001). Removal of Heavy Metals from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste. *Bioresource Technology*, **76,** 63 - 65.

Kalibantonga, P. D. (2005). *Adsorption of Heavy Metals from Solution by a South African Industrial Clay.* Master of Technology, Tshwane University of Technology.

Kannan, A.and Thambidurai, S. (2008). Comparative Studies on the Removal of Nickel (II) from Aqueous Solution by Using Carbon Derived from Palmyra Palm Fruit Seeds and Commercial Activated Carbon. *International Journal of Science & Technology,* **Volume 1,** 93-107.

Kawasaki, N., Bun-Ei, R., Ogata, F., Nakamura, T., Tanei, S.and Tanada, S. (2006). Water Treatment Technology Using Carbonaceous Materials Produced from Vegetable Biomass. *Journal of Water and Environment Technology*, **4,** 73-82.

Kazemipour, M., Ansari, M., Tajrobehkar, S., Majdzadeh, M.and Kermani, H. R. (2008). Removal of Lead, Cadmium, Zinc, and Copper from Industrial Wastewater by Carbon Developed from Walnut, Hazelnut, Almond, Pistachio, Shell, and Apricot Stone. *Journal of Hazardous Materials,* **150,** 322 - 327.

Khan, N. A., Ibrahim, S.and Subramaniam, P. (2004). Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents. *Malaysian Journal of Science,* **23,** 43 - 51.

Khantisuk, T. (2005). *Upgrading Coffee Ground Waste as Activated Carbon using Chemical Activation with Zinc Chloride and Potassium Carbonate.* Master of Science (Appropriate Technology for Resources and Environmental Development), Mahidoly Universit.

Khenniche, L.and Aissani, F. (2009). Characterization and Utilization of Activated Carbons Prepared from Coffee Residue for Adsorptive Removal of Salicylic Acid and Phenol: Kinetic and Isotherm Study. *Desalination and Water Treatment*, **11** 192–203.

Kiipper, H.and Kroneck, P. M. H. (2007). Nickel in the Environment and Its Role in the Metabolism of Plants and Cyanobacteria. *Met. Ions Life Sci.,* **2,** 31-62.

Kobya, M. (2004). Removal of Cr(VI) from Aqueous Solutions by Adsorption onto Hazelnut Shell Activated Carbon: Kinetic and Equilibrium Studies. *Bioresource Technology,* **91,** 317 - 321.

Kobya, M., Demirbas, E., Senturk, E.and Ince, M. (2005). Adsorption of Heavy Metal Ions from Aqueous Solutions by Activated Carbon Prepared from Apricot Stone. *Bioresource Technology,* **96,** 1518–1521.

Kondamudi, N., Mohapatra, S. K.and Misra, M. (2008). Spent Coffee Grounds as a Versatile Source of Green Energy. *J. Agric. Food Chem.,* **56,** 11757 - 111760.

Krishnan, K. A.and Anirudhan, T. (2003). Removal of cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies. *Water SA* **Vol. 29** 147 - 156.

Kumar, U. (2006). Agricultural Products and By-Products as a Low Cost Adsorbent for Heavy Metal Removal from Water and Wastewater: A Review. *Scientific Research and Essay* **Vol. 1** 033-037.

Kurniawan, T. A., Chan, G. Y. S., Lo, W. H.and Babel, S. (2006). Physico-Chemical Treatment Techniques for Wastewater Laden with Heavy Metals. *Chemical Engineering Journal,* **118,** 83 - 98.

Landner, L.and Reuther, R. (2004). *Metals in Society and in the Environment : A Critical Review of Current Knowledge on Fluxes, Speciation, Bioavailability and Risk for Adverse Effects of Copper, Chromium, Nickel and Zinc,* Dordrecht, Kluwer Academic Publishers.

Low, K. S., Lee, C. K.and Wong, S. Y. (2000). Metal Sorption Enhancement of Rice Hull Through Chemical Modification. *Environmental Technology,* **21,** 1239-1244.

Malaysia (2009). *Peraturan-Peraturan Kualiti Alam Sekeliling (Effluen Perindustrian) 2009.* P.U. (A) 434.

Malek, N. A. N. N.and Yusof, A. M. (2007). Removal of Cr(III) from Aqueous Solutions using Zeolite NaY Prepared from Rice Husk Ash. *The Malaysian Journal of Analytical Sciences,* **11** 76-83.

Masters, G. M. (1998). *Introduction to Environmental Engineering and Science 2nd Edition,* New Jersey, Prentice Hall.

Meena, A. K., Mishra, G. K., Rai, P. K., Rajagopal, C.and Nagar, P. N. (2005). Removal of Heavy Metal Ions from Aqueous Solutions using Carbon Aerogel as an Adsorbent. *Journal of Hazardous Materials,* **B122,** 161 - 170.

Mittal, A., Kaur, D.and Mittal, J. (2008). Applicability of Waste Materials—Bottom Ash and Deoiled Soya—as Adsorbents for the Removal and Recovery of a Hazardous Dye, Brilliant Green. *Journal of Colloid and Interface Science.*

Mondal, P., Majumder, C. B.and Mohanty, B. (2007). Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, ion and manganese from simulated ground water by Fe^{3+} impregnated activated carbon. *Journal of Hazardous Materials,* **150,** 695 - 702.

Moodley, K., Singh, R., Musapatika, E. T., Onyango, M. S.and Ochieng, A. (2011). Removal of Nickel from Wastewater Using an Agricultural Adsorbent. *Water SA* **Vol. 37**

Nieminen, T. M., Ukonmaanaho, L., Rausch, N.and Shotyk, W. (2007). Biogeochemistry of Nickel and Its Release into the Environment. *Met. Ions Life Sci.,* **2,** 1 - 22.

Nityanandi, D., Subbhuraam, C. V.and Kadirvelu, A. (2006). Adsorption of Nickel from Aqueous Solution by Coir Based Adsorbent, Puresorbe. *Environmental Technology,* **27,** 15-24

Nordberg, G. F., Fowler, B. A., Nordberg, M.and Friberg, L. T. (2007). *Handbook on the Toxicology of Metals,* London, Academic Press.

Oliveira, L. S., Franca, A. S., Alves, T. M.and Rocha, S. D. F. (2007). Evaluation of Untreated Coffee Husks as Potential Biosorbents for Treatment of Dye Contaminated Waters. *Journal of Hazardous Materials,* Article in Press.

Oliveira, W. E., Franca, A. S., Oliveira, L. S.and Rocha, S. D. (2008). Untreated Coffee Husks as Biosorbents for the Removal of Heavy Metals from Aqueous Solutions. *Journal of Hazardous Materials,* **152,** 1073-1081.

Parab, H., Joshi, S., Shenoy, N., Lali, A., Sarma, U. S.and Sudersanan, M. (2006). Detemination of kinetic and equilibrium parameters of batch adsorption of Co(II) and Ni(II) onto coir pith. *Process Biochemistry,* **41,** 609 - 615.

Patil, A. K.and Shrivastava, V. S. (2010). Adsorption of Ni(II) from aqueous solution on *Delonix regia* (Gulmohar) tree bark. *Archives of Applied Science Research,* **2,** 404 - 413.

Periasamy, K.and Namasivayam, C. (1995). Removal of Nickel (II) from Aqueous Solution and Nickel Plating Industry Wastewater using an Agricultural Waste : Peanut Hulls. *Waste Management,* **15,** 63 - 68.

Prasad, M., Xu, H.and Saxena, S. (2008). Multi-Component Sorption of Pb(II), Cu(II) and Zn(II) onto Low-Cost Mineral Adsorbent. *Journal of Hazardous Materials,* **154,** 221-229.

Rajalakshmi, R., Subashini, S.and Lalitha, P. (2009). Usefulness of activated carbon prepared from industrial wastes in the removal of nickel from aqueous solution. *E-Journal of Chemistry*, **6,** 361 - 370.

Ravenscroft, P., Brammer, H.and Richards, K. S. (2009). *Arsenic Pollution : A Global Synthethis*, West Sussex Wiley-Blackwell.

Rehman, M. S., Ahmad, N., Sawar, M.and Hussain, W. (2006). Pretreatment of Complex Industrial Wastewater by Ozonation. *Journal of Water and Environment Technology,* **4,** 52 - 59.

Richter, R. O.and Theis, T. L. (1980). Nickel Speciation in Soil/Water System. *In:* Nriagu, J. O. (ed.) *Nickel in The Environment.* Canada: John Wiley & Sons.

Sawyer, C. N., Mccarty, P. L.and G.F. Parkin (2003). *Chemistry for Environmental Engineering and Science 5th Edition,* New York, McGraw Hill.

Sengupta, A. K. (ed.) (2002). *Principles of Heavy Metals Separation: An Introduction,* Florida: Lewis Publishers.

Sharma, N.and Singh, J. (2007). Removal of Zn^{2+} Ions from Aqueous Solution Using Rice (*Oryza Sativa*) Husk in a Sequential Bed Adsorption Column. *In:* Sengupta, M.andR., D., eds. Taal 2007: The 12th World Lake Conference, 2007 Jaipur, India. 944 - 951.

Shuhaimi-Othman, M., Mushrifah, I., Lim, E. C.and Ahmad, A. (2008). Trend in Metals Variation in Tasik Chini, Pahang, Peninsular Malaysia. *Environ Monit Assess* **143,** 345–354.

Smith, A. W. (1985). Introduction. *In:* Clarke, R. J.and Macrae, R. (eds.) *Coffee Volume 1: Chemistry.* London: Elsevier Applied Science Publishers Ltd.

Spiller, M. A. (1998a). The Chemical Components of Coffee. *In:* Spiller, G. A. (ed.) *Caffein.* New York: CRC Press LLC.

Spiller, M. A. (1998b). The Coffee Plant and Its Processing. *In:* Spiller, G. A. (ed.) *Caffein.* New York: CRC Press LLC.

Sud, D., Mahajan, G.and Kaur, M. P. (2008). Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions – A Review. *Bioresource Technology* **99,** 6017–6027.

Sutherland, J. E.and Costa, M. (2002). Nickel. *In:* Sarkar, B. (ed.) *Heavy Metals in the Environment.* New York Marcel Dekker Inc.

Tan, W. T. (1985). Copper(II) Adsorption by Waste Tea Leaves and Coffee Powder. *Pertanika,* **8,** 223 - 230.

Tchobanoglous, G., Burton, F. L.and Stensel, H. D. (2004). *Wastewater Engineering Treatment and Reuse , Metcalf & Eddy, Inc.,* Singapore, McGraw-Hill.

Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J.and Tanada, S. (2005). Removal of Lead Ions in Drinking Water by Coffee Grounds as Vegetable Biomass. *Journal of Colloid and Interface Science* **281** 56–61.

Tolani, S., Mugweru, A., Craig, M.and Wanekaya, A. K. (2009). Rapid and Efficient Removal of Heavy Metal Ions from Aqueous Media Using Cysteine-Modified Polymer Nanowires. *Journal of Applied Polymer Science* **116,** 308–313

Utomo, H. D.and Hunter, K. A. (2007). Recycling Agricultural Waste Products for Sustainability: Coffee Waste for Heavy Metal Removal. *Ultrapure Water***,** 57-62

Utomo, H. D.and Hunter, K. A. (2010). Particle Concentration Effect: Adsorption of Divalent Metal Ions on Coffee Grounds. *Bioresource Technology,* **101** 1482–1486.

Wang, X. S., Huang, J., Hu, H. Q., Wang, J.and Qin, Y. (2007). Determination of kinetic and equlibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite. *Journal of Hazardous Materials,* **142,** 468 - 476.

Wasewar, K. L., Atif, M., Prasad, B.and Mishra, I. M. (2009). Batch Adsorption of Zinc on Tea Factory Waste. *Desalination,* **244,** 66 - 71.

Wintgens, J. N. (2004). *Coffee: Growing, Processing, Sustainable Production. A Guidebook for Growers, Processors, Traders and Researchers,* Germany, Wiley-VCH Verlag GmbH & Co.

Yao, P. (2010). *The Removal of Heavy Metal Pollutants With Electrowinning Techniques.* Doctor of Philosophy, Brown University.