NICKEL REMOVAL FROM ELECTROLESS WASTEWATER USING COAGULATION FLOCCULATION AND ION EXCHANGE

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Dedicated to my husband, daughter, siblings, nieces, mother in-law and beloved parents for their support, spirit, prayer and throughout any time of need.

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ABSTRACT

A massive growth in the industry of electroplating is associated with an increase in the quantity of nickel found in surface water and groundwater. This study focused on the removal of nickel concentration from organic solid waste stream of electroplating industry by using coagulation flocculation and ion exchange methods. In this study, various types of coagulants such as chitosan, WPC 6001, ferric chloride and polyacrylamide were tested to determine the best coagulant for removal of nickel, total suspended solid, chemical oxygen demand and turbidity. The effects of process variables such as pH and coagulant dosage on the performance of these coagulants were also investigated. Polyacrylamide (PAA) was found to be the best coagulant with percentage of 96.6%, 47.2%, 99.6% and 99.6% for removals of nickel, chemical oxygen demand, total suspended solid and turbidity respectively at the pH value of 10 and 1.6 mL/L dosage. From Response Surface Methodology (RSM), the optimal conditions for removal of nickel were found to be at pH 10.46 and 1.64 ml/L PAA dosage. Chelating resin was found to be the best resin with 99.6% nickel removal at pH value of 4. The treated wastewater's nickel content meets Standard A of the Malaysian Environmental Standard.

ABSTRAK

Pertumbuhan pesat dalam industri penyaduran dikaitkan dengan peningkatan dalam kuantiti nikel yang terdapat di permukaan dan air bawah tanah. Kajian ini memberi tumpuan kepada penyingkiran kepekatan nikel dari aliran sisa pepejal organik industri penyaduran dengan menggunakan kaedah pengentalan pengelompokan dan pertukaran ion. Dalam kajian ini, pelbagai ejen pengental seperti kitosan, WPC 6001, ferrik klorida dan poliakrilamida telah diuji untuk menentukan ejen pengental yang terbaik untuk penyingkiran nikel, permintaan oksigen kimia (COD), pepejal terampai dan kekeruhan. Kesan pembolehubah seperti pH dan dos pengental terhadap keberkesanan ejen pengental juga dikaji. Poliakrilamida (PAM) didapati merupakan ejen pengental yang terbaik dengan peratus penyingkiran 96.6%, 47.2% , 99.6% dan 99.6% bagi nikel, permintaan oksigen kimia, pepejal terampai dan kekeruhan pada nilai pH 10 dan 1.6 mL/L dos pengental. Dari *Response Surface Methodology* (RSM), keadaan optimum bagi penyingkiran nikel didapati pada pH 10.46 dan 1.64 mL/L dos pengental poliakrilamida. Resin pengkelatan merupakan resin yang terbaik dengan peratusan penyingkiran nikel 99.6% pada nilai pH 4. Air sisa yang dirawat kandungan nikelnya memenuhi piawaian A menurut Sistem Piawaian Alam Sekitar Malaysia.

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LIST OF ABBREVIATIONS

Al^{+3}	-	Aluminum ion
ANOVA	-	Analysis of variance
B	-	Beta
Cd	-	Cadmium
COD	-	Chemical oxygen demand
-COOH	-	Carboxylic acid
Cu	-	Copper
Cr(III)	-	Trivalent chromium
Co^{+2}	-	Cobalt
DBPs	-	Disenfection by products
EDTA	-	Ethylenediaminetetraacetic
EN	-	Electroless nickel
EPA	-	Environmental protection agency
Fe^{2+}	-	Ferrous
$FeCl_3$	-	Ferric chloride
HCl	-	Hydrochloric Acid
Hg^{+2}	-	Mercury
HPO^{2-}	-	Hypo
H^+	-	Hydrogen ion
MW	-	Molecular weight
Na^+	-	Sodium ion
NaCl	-	Sodium cloride
NaOH	-	Sodium hydroxide
Ni	-	Nickel
Ni-P	-	Nickel phosphorus

$-NH_2$	-	amino groups
NOM	-	Natural organic matter
NTU	-	Nephelometric turbidity units
NH_3^+	-	Ammonia ion
OH^-	–	Hydroxide ion
OS	-	Organic solid
OMG	-	Object Management Group
P	-	Phosphorus
PAA	-	Polyacrylamide
Pb	-	Lead
R-NH2	-	Primary weak base resin
$R\text{-}NHR_1$	-	Secondary weak base resin
$R\text{-}NR^1_2$	-	Tertiary weak base resin
RSM	-	Response surface methodology
R^2	-	Coefficient of determination
SAC	-	Strong acid cation
SBA	-	Strong base anion
SD	-	Standard deviation
SRWTP	-	Sacramento Regional Wastewater Treatment Plant
SO_3^-	-	Sulfite
S^{2-}	-	Sulfide
THM	-	Trihalomethane
TSS	-	Total suspended solid
WAC	-	Weak acid cation
WBA	-	Weak base anion

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The global latent demand for nickel, nickel-alloy wire, insulated wire and cable is estimated to be $0.6 billion in 2006. The distribution of world latent demand (potential industry earning) is not even across regions. The largest market is Asia, with $0.2 billion (31.86 percent), followed by North America and the Caribbean with $0.2 billion (25.67 percent) and Europe with $0.2 billion (25.16 percent) of the world market (Philip, 2005).

Ruelle (2010) reported that the mining firm Nickel Asia Corporation projected that nickel price will increase from the current $10.75-$10.85 to $11.90 per pound by the year 2012. Nickel is mainly used to produce rust-resistant stainless steel. Also, the demand of stainless steel rose to 9.1 million tons per year in the year 2012; hence the demand of raw nickel is growing by 8.5% annually in the same period. This figure can stipulate the quantities of nickel discharge to the aquatic environment. Thus, nickel contributes to the major surface water and groundwater contaminants.

Nickel pollution is invariably hazardous as the effluent contaminates the air, water and soil. Nickel pollution has deleterious effects on human health. According to the Environmental Quality (Industrial Effluent) Regulation of 2009, the effluent discharge under Standard A specification shall not exceed 0.2 mg/L (EQA, 2009). As a result, decreasing nickel concentration is necessary to reach permissible limits before it is discharged to the environment and to ensure that the effluent is within permissible levels.

The most commonly used methods of chemical treatment are precipitation and coagulation flocculation. The precipitation method can reduce soluble metal ions from a solution by producing metal hydroxides. The process is controlled by a simple pH adjustment. The pH is raised using an alkaline substance such as sodium hydroxide or lime. Then, the solution is converted into an insoluble form and it precipitates. Metcalf and Eddy (2003) reported that the general precipitation methods use hydroxides (OH^-) and sulfides (S^{2-}).

Beside chemical precipitation, Zhen Liang *et al*. (2009) reported that coagulation and flocculation are important processes in waste and wastewater treatment. Most commonly used as coagulant are aluminum based salts and iron based salts. Whereby in the removal of dissolved organic carbons, iron salts have been reported to be more effective than alum salts. This is followed by the flocculation process, where ferric chloride is added to wastewater which causes the colloidal material to destabilize and small particles to agglomerate by forming a large flock to settle (Amudaa and Amoob, 2007).

One well-known chemical coagulation and flocculation method uses chitosan. Chitosan is a biodegradable polymer, which is a non-toxic linear cationic polymer of high molecular weight and is more environment-friendly (Tan *et al*., 2007). Chitin, a cellulose material similar to biopolymer, is widely distributed in nature, found mainlyin marine invertebrates, fungi, insects and yeasts. Chitosan is a good choice as a coagulant because it is readily soluble in acid solutions (Mohd Ariffin *et al.*, 2008). Pan *et al.* (1999) reported that in various food wastes processing, chitosan is an effective coagulating agent for suspended solids. The high molecular weight (MW) of chitosan enhances the generation of bridging mechanisms (Roussy *et al.*, 2005).

There is a growing interest in the development of natural low-cost materials as an alternative to synthetic polyelectrolytes (Vijayaraghavan and Yun, 2008, Sharma *et al.*, 2006, Crini 2005). Numerous studies have proposed a biological product as an effective coagulation and flocculation agent (Maximova and Dahl, 2006, Deng *et al*., 2005). Wang *et al*. (2007) reported types of bioflocculants to include biopolymers such as starches, chitosan, alginates and microbial materials produced by microorganisms including bacteria, fungi and yeast. Bioflocculants are safe and biodegradable polymers and generate no secondary pollution; they are applicable in food, fermentation, and water and wastewater treatment. Due to public concerns of polyelectrolyte toxicity, it is believed that bioflocculants will be used more extensively (Bratby, 2007, Sharma and Dhuldhova, 2006, Crini, 2005).

1.2 Problem Statement

There is a steady increase in nickel-laden wastewater generated worldwide as a result of rapid industrialization. In the year 2000, 158,000 tons of nickel was used in the US, 13 % of which was consumed by the galvanic industry (Spoor, 2002). The annual growth of stainless steel demand has been estimated to increase by 9.1 million tons from the year 2009 to 2012. The result shows a growing demand for raw nickel to a tone of 8.5% annually for the same period (Ruelle, 2010). The contaminations that release into the water bodies can cause potential hazardous to aquatic, human health as well as the environment. Nickel has been identified to cause serious problems in humans such as allergy, dermatitis, sensitization and lung-nervous system damage; in fact, it has been placed on a list of thirteen hazardous metals by the US Environmental Protection Agency (Malkoc, 2006). Thus, it must be treated appropriately before being released into the environment.

At Seagate International (J) Sdn. Bhd, one of the heavy metals that are found to contaminate the wastewater is nickel. The current coagulation flocculation method is uneconomic, due to the in efficient removal of nickel despite using a high dosage of coagulants. The in efficient nickel removal from coagulation flocculation necessitates a subsequent treatment called ion exchange, and constant regeneration is needed. The level of nickel from exhausted ion exchange exceeds Malaysia's industrial effluent specification limit of Standard A (≤ 0.2 mg/L). This scenario may create an excursion condition to Seagate International (J) Sdn. Bhd. Therefore, the wastewater must be treated appropriately before it is discharged into municipal drains. The mean reading for nickel found in the wastewater are shown in Table 1.1.

Table 1.1 : Nickel content at subsequent sampling points

Parameter	**OS Influence (mg/L)**	**OS Effluent (mg/L)**	**Final Discharge (mg/L)**	**Standard A Specification (mg/L)**
Nickel	94.3	6.94	0.12 – 0.29	0.2

Note:

OS – Organic Solid

Chemical precipitation by coagulation and flocculation is an important process in waste and wastewater treatment. It is used to remove heavy metals such as nickel, suspended solids (SS), reduce chemical oxygen demand COD and turbidity (Amudaa and Amoob, 2007). Common coagulants include aluminum-based and iron-based salts. Other coagulants include commercial organic coagulants, polyacrylamide and chitosan, which is a biodegradable, non-toxic linear cationic polymer with a high molecular weight (Assaad *et al*., 2007; Ashoka *et al*., 2007; Mohd Ariffin *et al*., 2008). At neutral to alkaline pH, ferric salts will precipitate as an amorphous hydrated oxide or oxy-hydroxide, which has relatively stable and reproducible surface properties. The ability of the ferric hydroxide precipitate to absorb ions of heavy metals is characterized in single- and multi-adsorbate systems. Heavy metals could be absorbed as cations (Cr^{+3}, Pb^{+}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Cd^{+2}) in a neutral to high pH environment, and are absorbed as anions (SeO_2^{-2}, CrO_4^{-2}, $VO_3(OH)^{-2}$, AsO_4^{-3}) in a neutral to mildly acidic pH environment (Patoczka *et al*., 1998). Studies agree that ferric chloride is more effective than alum for capturing metals from wastewater. It is reported that the efficiency of ferric chloride outperformed alum in arsenic removal, with 96% of arsenic remove dusing ferric chloride compared to 81% when using alum salts (Johnson *et al*., 2008).

Studies have also shown that the effectiveness of coagulants is affected by dosage, pH and temperature. These factors need to be tweaked to obtain a high efficiency of treatment. The conventional method to seek optimal conditions is by trial and error approach, using jar tests. This involves changing the levels of one factor and at the same time, keeping the others constant, the running the experiment, observing the results and moving on to the next factor (Mohd Ariffin *et al*., 2008). This is indeed time and energy consuming. It is also usually incapable of revealing the optimal combination of factors, because it ignores the interaction among them (El Karamany, 2010; Trinh and Kang, 2011; Zheng *et al*., 2012). Moreover, a majority of wastewater treatment processes are contains multiple variables and optimization through the classical method is inflexible, unreliable and time-consuming (Bashir *et al*., 2012). A better alternative is the used of Respond Surface Methodology (RSM) because it includes the influences of individual factors as well as the influences of their interaction. RSM is a technique for designing experiments and building models which evaluates the effects of several factors to achieve optimum conditions for desirable responses with a limited number of planned experiments (Cristian *et al*., 2010; Raissi *et al*., 2009; Zheng *et al*., 2012). There are published RSM studies that focuses on the usability of RSM for optimization of various types of wastewater treatment processes (Bashir *et al*., 2012; Trinh and Kang, 2011; Zheng *et al*., 2012).

However, it is observed that works concerning the optimization of nickel removal using chitosan are not readily available.

1.3 Research Objective

The main objectives of this research are outlined below.

- To determine the performance of coagulants (chitosan, WPC6001, ferric chloride and polyacrylamide) in the removal of nickel from wastewater.
- To determine the effects of coagulant dosage and pH on the performance of these coagulants.
- To optimize performance of the best coagulant by using RSM.
- To determine the performance of ion exchange (strong acid cation and chelating resin) on the nickel removal process.

1.4 Research Scope

The scope of this research includes:

- The study is carried out in a lab-scale operation which utilized the actual electroless wastewater by analyse the characterization as the influent.

- Study the nickel, COD, TSS and turbidity removal efficiency of the various coagulants (chitosan, WPC6001, ferric chloride and polyacrylamide (PAA)) at different pH levels(4 – 11) and coagulant dosages.
- Evaluating the optimum pH and coagulant dosage for PAA using response surface methodology (RSM).
- Study the performance of different ion exchange (strong acid cation and chelating resin) on nickel removal at pH 4.
- Evaluate the operation condition for chelating resin at different pH and contact time.

1.5 Significance of The Study

Large quantities of trace metals such as nickel are discharged from various industrial processes into the environment; endanger humans as well as flora and fauna. Growing public concern about environmental protection/sustainability and public health has led to the enactment of environmental laws and environmental standards being set up. Therefore, to meet these standards, there is an urgent need for manufacturers to minimize release of these metallic pollutants into bodies of water by treating the wastewater prior to discharging it into the environment.

This has prompted more researches to be conducted to find more efficient ways to remove these nickels from the wastewater before being released into the environment. Therefore, the result from this research will serve as a guide to treat wastewater for electroless industries, regulatory bodies and policymakers.

1.6 Organization of the Thesis

This thesis consists of five chapters. Each chapter gives information about a specific research area.

- **Chapter 1** details the research background, research aim and objectives as well as the scope of the study.

- **Chapter 2** reviews literature on general information on nickel, electroless plating industry wastewater, coagulation-flocculation method and ion exchange.

- **Chapter 3** covers a general description of the experimental setup and the procedures in carrying out the research work. It includes: sample collection and characterization, assessment of nickel removal efficiency by different coagulants, assessment of nickel removal efficiency by different ion exchange resins and determination of optimum operating conditions for chemical precipitation using response surface methodology (RSM).

- **Chapter 4** presents and discusses the results of the research. It includes the effect of pH and coagulant dosage on the efficiency of nickel removal. The performances of various ion exchange resins are discussed. Finally, the results of the optimization process using RSM is presented.

- **Chapter 5** deals with conclusions and recommendations. It presents the conclusions derived from this research study and recommendations for future studies.

REFERENCE

Ahmad, A. L., Sumathi, S. and Hameed, B.H. (2006). Coagulation of Residue Oil and Suspended Solid in Palm Oil Mill Effluent by chitosan, Alum and PAC. *Chemical Engineesing Journal*, 118: 99-105

Ali, Z.A., Venkatesan., J., Kim, S.K., Sudha, P.N. (2011). Beneficial effect of chitosan-g-polyacrylamide copolymer in removal of heavy metal from industrial dye effluents. *International Journal of Environmental Science*. 1(5). 820 – 833.

Alyuz B, Veli S. (2009). Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *Journal of Hazardous Materials*, 167:482–488.

Altmayer, Frank (2000). *Nickel Plating AESF Training Course*: Electroplating and Surface Finishing, Vol 1.

Amudaa, O. S. and Amoob, I.A. (2007). Coagulant/Flocculation Process and Sludge Conditioning in Beverage Industrial Wastewater Treatment. *Journal of Hazardous Material*. 141, 778 – 783.

Anderson, M. and Whitcomb, P. J. (2005). *RSM simplified: Optimizing process using response surface methodology for design of experiments. Productivity Press*, New York.

Anderson, M. and Whitcomb, P. J. (2007) *DOE simplified : Practical Tools for Effective Experimentation. Productivity Press.* (2nd ed.) New York.

Anirudhan, T.S., Suchithra, P.S. (2009). Adsorption characteristics of humic acid-immobilized amine modified polyacrylamide/bentonite composite for cationic dyes in aqueous solution. Journal of Environmental Sciences. 21, 884 – 891.

Anthony Ma, T. H., Shek, S. J., Allen, V. K. C., Lee, G. and McKay (2008). Removal of Nickel from Effluent by Chelating Ion Exchanges. Department of

Chemical Engineering, Hong Kong. University of Science and Technology Clear Water, bay Kowloon, Hong Kong.

Andrei, A. Zagorodni (2007). *Ion Exchange Materials Properties and Applications.* Amsterdam, Netherlands. Elsevier.

APHA (American Public Health Association)(2005). Standard Methods for the Examination of Water and Wastewater,. 21st ed. Washington, D.C.

Ariffin, A. Shatat, R.S., Nik Norulaini, a.R. and Mohd Maor, A.K. (2005). Synthetic Polyelectrolytes of Varying Charge Densities but Similar Molar Mass Based on Acrylamide and Their Application o Palm Oil Mill Effluent Treatment. *Desalination* 173. 201-208

Argun ME (2008). Use of clinoptilolite for the removal of nickel ions from water: kinetics and thermodynamics. *Journal of Hazardous Materials*, 150,587–595.

Arslan-Alaton, I, Turell, G., and Olmez-Hanci,T. (2009). Treatment of azo dye production wastewater using Photo-Fenton-like advance oxidation process: Optimization by response surface methodology. *Journal of Photochemistry and Photobiology A: Chemistry*, 202, 142-153.

Ashmore, M. H. and Hearn, J. (2000). Flocculation of Model Latex Particles by Chitosan of Varying Degree of Acetylation Langmir, 16: 4906-4911.

Ashoka Gamage and Fereidoon Shahidi (2007). Use of chitosan for the Removal of Metal Ion Contaminants and Proteins from Water. *Food Chemistry*. 104(3), 989–996.

Assaad, E., Azzouz, A., Niztor, D., Ursu, A. V., Sajin, T., Miron, D. N., Monette. F., Niquette, P. and Hauster, R. (2007). Metal Removal Through Synergic Coagulation-Flocculation Using an Optimized Chitosan-Montmorillonite System. *Applied Clay Science*. 37, 258- 274.

Babel, S., Kurniawan, T. A. (2003), Low-Cost Adsorbents for Heavy Metal Uptake from Contaminated Water: A Review. *Journal of Hazardous Materials*, B97, 219.

Bae, H.Y., Kim, H.J., Lee. E.J., Sung, N.C, Lee, S.S., Kim, Y.H. (2007) Potable Water Treatment by Polyacrylamide Base Flocculants, Coupled with an Inorganic Coagulant. *Environ. Eng. Res*. 12(1). 21-29.

Barnes, D., Bliss, P. J., Gould, B.W. and Vallentina, H. R. (1981). *Water and Wastewater Engineering System*. London : Pitman Book Limited.

Bashir, M.J.K., Abdul Aziz, H., Aziz, S.Q. and Abu Amr, S. (2012). An overview of wastewater treatment processes optimization using response surface methodology (RSM). The 4th International Engineering Conference –Towards engineering of 21st century, Malaysia. 1-11.

Benjamin, M. M. (1983). Adsorption and Surface Precipitation of Metals on Amorphous Iron Oxyhydroxide. *Environ. Sri. Technol*. 17(11). 686 – 692.

Bough, W. A., Landes, D. R., Miller, J., Young, C. T. and McWhorte, T. R. (1976). Utilization of Chitosan for Recovery of Coagulated By-Products from Food Processing Wastes and Treatment Systems. California: *Proceedings of the Sixth National Symposium on Food Processing Wastes*. 9-11 April. Madison, Wisconsin.

Bratby, J. (2007) *Coagulation and Flocculation in Water and Wastewater Treatment 2nd ed*. London: International Water Association (IWA) Publishing

Chang, I.S, Kimb, B.H. and Shin, P.K. (1997). Use of sulfide and hydrogen peroxide to control bacterial contamination in ethanol fermentation. *Applied and Environmental Microbiology*. 63(1), 1-6.

Cohen Stuart, M. A. and Fleer, G. J. (1996). Adsorbed polymer layers in Nonequilibrium Situations. *Annual Reviews of Materials Science 26*, 463–500. *Colloids and Surfaces.* A 147(13), 359-364.

Cornell, J. A (1990) *How to Apply Response Surface Methadology, Revised Edition* (Vol 8). Tammy Griffin, United State of America : Book Crafters.

Cornell, J. A. *How to Apply Respond Surface Methodology*. 2nd edition. West Wisconsin Avenue Milwaukee, U.S. 1990

Crini, G. (2005). Recent Developments in Polysaccharide-Based Materials Used as Adsorbents in Wastewater Treatment. *Prog Polym Sci*. 30, 38–70.

Cristian, J.B.D, Luciana, F.C. and Jonas, C. (2010). The Use of Response Surface Methodology in Optimization of Lactic Acid Production: Focus on Medium Supplementation, Temperature and pH Control. Food Technology and Biotechnology. 48 (2), 175–181.

Coman, V., Robotin, B. and Ilea, P. (2013). Nickel Recovery/Removal from Industrial Wastes: A Review. *Journal Resources, Conservation and Recycling*. 73, 220 – 238.

Cussler, E.L. (1984). Mass Transformer in Fliud Systems. *Cambridge University Press*. Cambridge, UK.

Dabrowski, A., Hubicki, Z., Podko, P. and Roben E. (2004). Flocculation of Kaoline Suspensions in Water by Chitosan. *Water Research*. 35, 3904-3908.

Das, K. K. and Somasundaran, P. (2004). A Kinetic Investigation of the Flocculation of Alumina with Polyacrylic Acid. *Journal Colloid Interference Science*. 271(1), 102-109.

David, J., Kunces and Willian, Toller , H. (1985). Waste Treatment of Electroless Nickel to Remove Heavy Metal , Phosphites and Chelator

Dave, R.S., Dave, G.B., Mishra, V.P. (2011). Removal of Nickel from Electroplating wastewater by weakly basic chelating anion exchange resins; Dowex 50x4, Dowex 50x2 and Dowex M-4195. *Journal of Applied Science in Environmental Sanitation*. 6(1) 39-44.

De, B.R, Koyya, H., Tripathy, T. (2010) Synthesis of Hyrdoxyethyl Starch-gpolyacrylamide (HES-g-PAM) and its Application in Removal of Heavy Metal Ions. *Journal of Physical Science*. 4. 199-205

Deng, S., Yu, G., Ting, Y. P. (2005). Production of a Bioflocculant by Aspergillus Parasiticus and its Application in Dye Removal. *Colloids Surf B Biointerfaces.* 44, 179–86.

DeSilva, F.J. (1999) Essential of Ion Exchange. *25th Annual WQA Conference*. March 17

Dietrich, T.H. (1998). *Heavy Metal from Dilute Aqueous Streams by the use of Ion-exchange resin.* Master Degree in Technology (Chemical Engineering). Cape Peninsula University of Technology.

Divakaran, R. and Pillai, V. N. S. (2001). Flocculation of Kaolinite Suspensions in Water by Chitosan. *Water Research*. 35(16), 3904-3908.

Domard, A., Rinaudo, M. and Terrassin, C. (1989). Adsorption of Chitosan and Quarternized Derivative on Kaoline. *Journal Applied Polymer Science*. 38, 1799 – 1806

Eaton, A.D., Cleseri, L.S, Greenberg, A.E. (1995) *Standard Metods for the Examination of Water and Wastewater*. Washington, D. C. American Public Health Assoc.

Eckenfelder, W. W., Jr. (2000) *Industrial Water Pollution Controls*. 3rd Edition, McGraw-Hill Companies, Inc. United States.

El Karamany, H. (2010). Study for industrial wastewater treatment using some coagulants. Fourteenth International Water Technology Conference, IWTC 14 2010, Cairo, Egypt. 283-291.

Elshazly, A.H., Konsowa, A.H. (2003). Removal of nickel ions from wastewater using cation-exchnage resin in a batch-stirred tank reactor. *Conference on Desalination and the Environmental: Frest Water for All, Malta*. 4 – 8 May 2003, European Desalination Society, International Water Association.

Eric Dickinson (1989). A Model of a Concentrated Dispersion Exhibiting Bridging Flocculation and Depletion Flocculation. *Journal of Colloid and Interface Science*. 132 (1), 274-278.

Evans, J. R., Davids, W. G., MacRae, J. D. and Amirbbahman, A. (2002). Kinetics of Cadmium Uptake by Chitosan-Based crab Shells. *Water Research*. 36: 3216-3226.

Field and William, D. (1982). *Electroless Nickel Plating in Metals Handbook - Volume 5*. Metal Park, OH: American Society for Metals.

Fleer, G. J., Cohen Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T. and Vincent, B. (1993). *Polymers at Interfaces*. New York : Chapman & Hall, Inc.

Franceschi, M., Giroua, A., Carro, A. M., Mauretteb, M. T. and Puech, C. E. (2002). Optimization of the Coagulation-Flocculation Process of Raw Water by Optimal Design Method. *Water Research*. 36. 3561-3572.

Gamage, D. A. S. (2003). *The Used of Chitosan for the Removal of Metal Ions contaminants and Proteins from Water*. Master of Science. Memorial University of Newfoundland.

Guerrero, L., Omil, F., Mendez, R. and Lema, J.M. (1998). Protein Recovery During the Overall Treatment of Wastewater from Fish-Meal Factories, *Bioresourse Technology*. 63(3), 221-229.

Guibal, E. and Roussy, J. (2007). Coagulation and Flocculation of Dye-Containing Solutions Using a Biopolymer (Chitosan). *Reactive and Functional Polymers.* 67. 33-42.

Guzman, J., Saucedo, I., Revilla, J., Navarro, R., and Guibal, E. (2003)). Copper Sorption by Chitosan in the Presence of Citrate Ions: Influence of Metal Speciation on Sorption Mechanism and Uptake Capacities. *International Journal of Biological Macromolecules*. 33. 57-65

Goh, C.S., Lee, K.T., Bhatia, S., (2010). Hot compressed water pretreatment of oil palm fronds to enhance glucose recovery for production of second generation bioethanol. Bioresour. Technol. 101, 7362–7367.

Hamidi, A., Aziz, Mohd, N. Adlan, Kamar, S., Ariffin (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(6) ,1578–1583.

Hao, Y., Yang, X. H., Zhang, J., Hong, J., Hong, X. and Ma, X. L. (2006). Flocculation Sweep a Nation. *Pollution Engineering.* 38, 57-65.

Helfferich, F. G. (1962). Ion Exchange, *Science American Association Advancement of Sciences (AAAS)*, 138 (3537), 133 l

Helfferich, T., *Ion exchange*, McGraw-Hill Book Company, Inc, 1995.

Henry and James R. (2000) Electroless (Autocatalytic) Plating. *Metal Finishing Guidebook*. 98 (1), 424-435

Hoffland Environmental Inc. (2006). *Hydroxide Precipitation*. www.hofflandenv.com

IAEA (2000). Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers, Technical Reports Series No. 408. *International Atomic Energy Agency (IAEA),* Vienna

Inukai, Y., Tanaka, Y., Matsuda, T., Mihara, N., Yamada, K., Nambu, N., Itoh, O., Doi, T., Kaida, Y. and Yasuda, S. (2004). Emoval of Boron (III) by N-methylglucamine Type Cellulose Derivatives With high Adsoprtion Rate . *Analytica Chimica Acta.* 511, 261-265.

Juzek, P., Russell, K. J., John, J. S., (1998). Trace Heavy Metal Removal with Ferric Chloride. *Water Environmental Federation Industrial Water Technical Concerence*. Nashville, TN.

Johnson, P.N. and Amirtharajah, A. (1983) Ferric Chloride and Alum as Single and Dual Coagulants. *Journal of The American Water Works Association*. 75(5): 232-239.

Johnson, P.D., Girinathannair, P., Ohlinger, K.N, Ritchie, S., Teuber, L., Kirby, J. (2008). enhanced Removal of Heavy Metal in Primary Treatment Using Coagulation and Flocculation. *Water Environ. Res*, 80(5), 472 – 479.

Kesraoui-Ouki, S., Cheeseman, C. and Perry, R. (1994). Natural Zeolite Utilization in Pollution Control: A Review of Applications to Metals Effluents, *J. Chem. Technol. Biotechnol*. 59,121–126.

Kocaoba, S., Orhan, Y., and Akyüz, T. (2007). Kinetic and Equilibrium Studies of Heavy Metal Ions Removal by Use on Natural Zeolite. *Desalination*. 214. 1-10.

Kumar, P.S., Ramakrishnan,K., Gayathri, R. (2010) Removal of Nickel (III) from Aqueous Solution by Ceralite IR 120 Cationic Exchange Resins. *Journal of Engineering Science and Technology*. 5(2). 232-243.

Lima, I. S. and Airoldi, S. (2004). A Thermodynamic Investigation on Chitosan-Divalent Cation Interactions. *Thermochimica Acta*. 42(1), 133-139.

Macro, A. B., Ricardo, E. S., Eliane P. O., Leonardo, S.V., and Luciane, A. E. (2008). Response Surface Methodology (RSM) as a tools for optimization in analytical chemistry. *Journal of Elservier Talanta*. 76(2), 965-977

Malaysia (2009) Environmental Quality Act (Industrial Effluent) Regulation. P.U. (A) 434. 2009

Malkoc, E. (2006). Ni(II) Removal from Aqueous Solutions Using Cone Biomass of Thuja Orientalis. *Journal of Hazardous Materials* .137(2), 899-908.

Malliou, E., Loizidou, M., Spyrellis, N. (1994). Uptake of lead and Cadmium by Clinoptilolite. *Sci. Total Environ*. 149, 139–144.

Mayer, R. H., Montgomery, D. C. *Response Surface Methodology*. Wiley: New York, 2002

Maximova, N. and Dahl, O. (2006). Environmental Implications of Aggregation Phenomena: Current Understanding. *Curr Opin Colloid Int Sci*. 11(4), 246–66.

Metcalf and Eddy (2003). Wastewater Engineering : Treatment and Reuse (4^{th} ed.). New York : McGraw-Hill Companies, Inc.

Mohd Ariffin, A., Lim S. H., Zainura N. and Zaini U. (2008). Removal of Boron Industrial Wastewater by Chemical Precipitation Using Chitosan. Journal of Chemical and Natural Resources Engineering. 4(1), 1-11.

Moudgil, B. M. and Somasundaran, P. (1985). *Flocculation Sedimentation and Consolidation*. United States of America: Engineering Fondation.

Moudgil, B. M., Behl , S. and Matis, E. D. (1995). *Flotation Science and Engineering,* New York : Marcel Dekker Inc .

Mousavi, H.Z., Hosseinifair, A. and Jahed, V. (2012). Study of the adsorption thermodynamics and kinetics of Cr(II) and Ni (II) removal by polyacrylamide. *J. Serb. Chem. Soc.* 77 (3) 393–405.

Muthuvelayudham, T and Viruthagiu, T. (2000). Application of Central Composite Design Base Response Surface Methodology in Paramter Optimization and on Cellulase Production Using Agricultural Waste. Internation Journal of Chemical and iological Engineering 3(2), 97-104.

Nadir Dizge, Bulent Keskinler and Hulusi Barlas (2009). Sorption of Ni (II) ions from Aqueous Solution by Lewatit Cation-exchange Resin. *Journal of Hazardous Material* 167 (1-3), 915-926.

Napper, D.H. (1983). *Polymeric Stabilization of Colloidal Dispersions.* London : Academic Press.

Naushad, Mu. (2009). Inorganic and Composite Ion Exchange Material and their Application. *Ion Exchange Letter*, 2, 1-14.

Nurzihan, S. (2010). *Selective Removal of Heavy Metal from Electroplating Industrial Wastewater Using Ion Exchange Process.* Bachelor of Civil Engineering., Universiti Teknologi Malaysia, Skudia

Ohlinger, N. K. (1993) Enhanced Primary Treatment Using Chemical Addition. M.S. Thesis, California State University, Sacramento.

OMG Electronic Chemicals (2007), *General Plating Process Module #1.* Object Management Group, Inc.

Ortege, E. C., Cheeseman, C., Knight, J., Loizidou, M. (2000). Properties of Alkali-activated Clinoptilolite. *Cement Concrete Res* 30(10), 1641–1646.

Pan, J. R., Huang, C. P., Chen, S. C. and Chung, Y. C. (1999). Evaluation of a Modified Chitosan Biopolymer for Coagulation of Colloidal Particles.

Papadopoulos, A., Fatta, D., Perperis, K., Mentzis, A., Haralambous. K.J. and Loizidou, .M . (2004). Nickel Uptake from a Wastewater Stream Produced in a Metal Finishing Industry by Combination of Ion-exchange and Precipitation Methods. *Separation and Purification Technology* . 39(3), 181–188

Papadopoulos, A., Kapetanios, E., Loizidou M. (1996). Studies on the Use of clinoptilolite for Ammonia Removal from Leachates, *Journal Environ. Sci. Health. Part A : Environ. Sci Eng. Toxic Hazard*. Subst. Control. 31, 211 – 220.

Paul Chen, J., Yang, L., Wun, J. N., Wang, Lawrence K., and Sook, L. T. (2006). Advanced Pyhsicochemical Treatment Process. In: Wang, Lawrence K. ed. Handbook ogf Environmental Engineering Volume 4. Totowa: Humana Press. 261-289: 2010.

Patoczka, J., Johnson, R. K., Scheri, J. J.. (1998) Trace Heavy Metal Removal with Ferric Chloride. *Water Environment Federation Industrial Wastes Technical Conference*. Nashville TN.

Pen-Chi Chinag, E. E., Chang, Pin-Cheng Chang and Chin-Pao Huang (2009). *Effects of Pre-ozonation on the Removal of THM Precursors by Coagulation.* Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan, ROC

Philip A Schweitzer (1979) *Handbook of Separation Techniques for Chemical Engineers*, New York : Mc Graw Hill, Inc.

Philip, M. Parker (2005). The 2006 – 2011 World Outlook for Nickel and Nickel Alloy Wire and Insulated Wire and Cable. *World Outlook* Report. Business, Innovation and Society INSEAD (Singapore and Fontainebleau) France.

Pinotti, A., Bevilacqua, A. and Zaritzky, N. (1997). Optimization of the Flocculation Stage in a Model System of a Food Emulsion Waste using Chitosan as Polyelectrolyte. *Journal of Food Engineering*. 32(1), 69-81.

Poon, C. S.; Chu, C. W. (1999) The Use of Ferric Chloride and Anionic Polymer in the Chemically Assisted Primary Sedimentation Process. *Chemosphere*, 39 (10), 1577–1582.

Raisssi, S. (2009). Developing New Processes and Optimizing Performance Using Response Surface Methodology. World Academy of Science, Engineering and Technology. 25, 1039-1042.

Ramandi, N. F., Najafi, N. M., Raofie, F. and Ghasemi, E. (2011). Central Composite Design for the Optimization of Supercritical Carbon Dioxide Fluid Extraction of Fatty Acids from Borago Officinalis L. Flower. *Journal of Food Science*, 76(9), C1262-C1266. doi: 10.1111/j.1750-3841.2011.02394.x

Remco Engineering (1981). Control and Treatment Technology for the Metal Finishing Industry – Ion Exchange. *Summary Report.* USEPA EPA 625-81-007.

Renault, F., Sancey, B., Badot, P. M., Crini, G. (2009). Chitosan for Coagulation / Flocculation Process - An Eco-Friently Approach. *European Polymer Journal* 45, 1337-1348.

Rigas F**,** Panteleos P**,**Laoudis C(2010). Central composite design in refinery's wastewater treatment by air flotation. *Global NEST: The International Journal 2 (3)*,245-253.

Roberts, G. A. F (1992). *Solubility and Solution Behaviour of Chitin and Chitosan*. In: Roberts G. A. F. *Chitin Chemistry*. Houndmills UK : MacMillan Press Ltd.

Roussy, J., Vooren, M. V., Dempsey, B. A. and Guibal, E. (2005). Influence of Chitosan Characteristics on the Coagulation and the Flocculation of Bentonite Suspensions. *Water Research*. 39 (14), 3247 – 3258.

Ruelle Albert D. Castro (2010, October 26). Rising metal price underpins: Nickel Asia growth. *Malaya Business Insight*. Retrieved October 26, 2010, from http://www.malaya.com.ph

Russell V.Lenth. (2009). Response-Surface Methodology in , Using RSM. *Journal of Statistical Software*, 7(32), 1-17. American Statistical Association

Savant, V.D. and Tores, J.A. (2000). Chitosan-Based Coagulation Agents for Treatment Cheddar Cheese Whey. *Biotechnology Progress*. 16,1091-1097.

Schmuhl, R., Krieg, H. M. and Keizer, K. (2001). Adsorption of Cu(II) and Cr (IV) Ion by Chitosan: Kinetics and Equilibrium Studies. *Water S.A*. 27 (1), 1-7.

Scott, N. K., Green, J. F., Do, H. D., McLean, S. J. (1995) Arsenic Removal by Coagulation. *J. Am. Water Works Assoc.*, 87 (4), 114–126.

Seagate (2007). Waste water treatment system. *The proposed substrate plant for Seagate International (Johor) Sdn. Bhd.* Vol 1 of 3, 5-15

Sharma, B. R., Dhuldhoya, N. C. and Merchant, U. C. (2006). Flocculants-an ecofriendly approach. *Journal of Polymers and the Environment* 14, 195–202.

Sharna, M., Glover, Yao-de Yan, Graeme J., Jameson and Simon Biggs. (2000) Bridging flocculation Studied by Light Scattering and Settling. *Chemical Engineering Journal*, 80(1), 3-12.

Shawabkeh, R., Al-Harahsheh, A., Hami, M., and Khlaifat, H. A. (2004). Conversion of soil shale ash into zeolite for cadmium and lead removal from wastewater. *Fuel* , 83(7-8), 981-985.

Sletten, R. S., Benjamin, M. M., Horng, J. J. and Ferguson, J. F. (1995). Physical–Chemical Treatment of Landfill Leachate Formetals Removal. *Water Research*. 29, 2376-2386.

Sridevi, M., Genitha, Er TR. (2012). Optimization of Osmotic Dehydration Process of Pineapple by Response Surface Methodology. *J. Food Process Technol*. 3. 173

Stechemesser, H. and Dobias, B. (2005). Coagulation and flocculation. *Surfactant Science Series*. 126(2nd ed). CRC Press.

Stephenson, R. J. and Duff, J. B. (1996). Coagulation and Precipitation of Mechanical Pulping Effluent, 2 – Toxicity Removal and Metal Salt Removal. *Water Research*. 30(4) 793 – 798.

Strand, S. P., Varum, K. M. and Φstgaard, K. (2003). Interactions between Chitosan and Bacteria Suspensions: adsorption and Flocculation. *Colloids and Surface B: Biointerfaces*. 27, 71-81

Spoor, P.B. (2002). Removal of nickel ions from galvani wastewater streams using a hybrid ion exchange – electrodialysis system. A Phd thesis, Technical university Eindhoven, Canada.

Suresh, K. Sahni and Jan Reedijk (1984). Coordination Chemistry of Chelating Resins & Ion Exchanges. *Coordination Chemistry (*59), 1-139.

Tan Pei Li, Mohd Ariffin Abu Hassan, Zainura Zainon Noor (2007). Coagulation and Flocculation Treatment of Wastewater in Textile Industry Using Chitosan. *Journal of Chemical and Natural Resources Engineering.* 4(1), 43-53.

Tatsi, A. A., Zouboulis, A. I., Matis, K. A. and Samaras, P. (2003). Coagulation-Flocculation Pretreatment of Sanitary Landfill Leachates. *Chemosphere*. 53, 737-744.

Trinh, T.K. and Kang, L.S. (2011). Response surface methodological approach to optimize the coagulation–flocculation process in drinking water treatment. Chemical engineering research and design. 89, 1126-1135.

United States Environmental Protection Agency (USEPA) (1992). Guides to Pollution Prevention. *The Metal Finishing Industry*. Washington DC : USEPA.

Van de Ven and Theo, G. M. (1994). Kinetic Aspects of Polymer and Polyelectrolyte adsorption on Surfaces. *Advances in Colloid and Interface Science*. 48, 121–140.

Venugopal B, Luckey T (1975) Toxicity of non radioactive heavy metals and their salts. In: Coulston F (ed) Heavy metal toxicity, safety and hormology. Academic/George Thieme Stuttagart, New York

Vijayaraghavan, K. and Yun, Y. S. (2008). Bacterial Biosorbents and Biosorption. *Biotechnol Adv*. 26(3), 266–291.

Vishnu, P., Madhabhai, P., Rakesh, P. (2005). Chitosan : A Unique Pharmaceutical Excipient. Pharmaceutical Technology at Shree S.K. Patel college of Pharmaceutical Education and Research, Ganpat Vidyanagar, India.

Wang, H. C., Li, M. H., Tsang, H. W., Wu, M. M. and Lin, H. P. P (2007). *U. S. Patent No. 20070062865* . Novel Biological Flocculants and Production Methods.

Weber, W. J. (1972). *Physicochemical Process for Water Quality Control*. New York : John Wiley and Sons.

Weisenberger, L. M. (1982). *Metal Handbook Volume 6*. American Society of Metal :Metal Park, OH

Wong, S.S., Teng, T.T., Ahmad, A.L., Najafpour, G. (2006). Treatment of pulp and aper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation. *Journal Hazard Mater*. 135(1-3). 378-388.

Ya'aini, N., Saidini Amin N. A., Asmadi, M. (2012) Bioresource Technology. Optimization of levulinic acid from lignocellulosic biomass using a new hydrid catalyst. *Bioresource Technology*. 116 58-65.

Yang, T.H. (2008) Recent Application of Polyacrylamide as Biomaterials. *Recent Patents on Material Science*. 1. 29-40

Zhao, W., Ting, Y. P., Chen, J. P., Xing, C. H. and Shi, S. Q. (2000). Advanced primary treatment of wastewater using a bio-flocculation–adsorption sedimentation process. *Acta Biotechnol.* 20 , pp. 53–64.

Zhen Liang, Yanxin Wang, Yu Zhou and Hui Liu (2009). *Coagulation removal of melanoidins from biologically treated molasses wastewater using ferric chloride*. Biogeology and Environmental Geology and School of Environmental Studies, China University of Geosciences, Wuhan, China

Zheng, H., Tshukudu, T. and Yang, J. (2012). Optimization of the Coagulation-flocculation Process for WastewaterTreatment Using Polymeric Ferric Sulfate (PFS) - Poly-diallyldimethyl Ammonium Chloride (PDADMAC) Composite Coagulant. Hydrology current research. 3(4), doi.org/10.4172/2157-7587.1000139.