PREPARATION AND CHARACTERIZATION OF SUPPORTED NANO-ZERO VALENT IRON FOR TREATMENT OF ORGANIC POLLUTANTS IN WATER

ATYAF KHALID HAMMED AL-DAHAN

DOCTOR OF PHILOSOPHY

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy in Chemistry.

____

(Supervisor's Signature)

Full Name : DR. MOHD HASBI BIN AB. RAHIM

Position : ASSOCIATE PROFFESOR

Date : 2017

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

____

(Student's Signature)

Full Name : ATYAF KHALID HAMMED AL-DAHAN

ID Number : PSK13006

Date : May 2017

PREPARATION AND CHARACTERIZATION OF SUPPORTED NANO-ZERO VALENT IRON FOR TREATMENT OF ORGANIC POLLUTANTS IN WATER

ATYAF KHALID HAMMED AL-DAHAN

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Doctor of Philosophy

Faculty of Industrial Sciences & Technology

UNIVERSITI MALAYSIA PAHANG

MAY 2017

DEDICATION

To

My Father and my younger sister Spirits in heaven and my beloved Mother

In Recognition of Their Worth, Love, and Respect

My brothers

My sisters

My friends

ACKNOWLEDGEMENTS

In the name of Allah Most merciful Most Compassionate and prayer on Muhammad. I would like to express my deep appreciation and gratitude to my supervisors. I'm deeply indebted to my supervisor Assoc. Prof. Dr. Mohd Hasbi Bin Ab. Rahim who guided me in every possible way with his experience, motivation, and his positive attitude.

I'm also very grateful to Prof. Dr. Mohd Ridzuan Bin Nordin for his continuous help and advice during my research work and I'm also very grateful to Dr. Nugroho Dewayanto for his continuous help, encouragement and positive attitude.

I would like as well to thank the department of the Universiti Malaysia Pahang, especially the Faculty of Industrial Sciences & Technology for giving me the opportunity to complete my study.

I feel responsible for thanking the Ministry of Science and Technology, Department of Environment and Water, Iraq for their supports. Finally, I'm deeply indebted and grateful to My Father and my younger sister Spirits in heaven and my beloved Mother, my brothers, my sisters and my friends for their moral support.

Atyaf Khalid Hammed Al-Dahan

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

q_e	Uptake of adsorbate at equilibrium time
C_e	The final concentration (mg/L)
C_i	The initial concentration (mg/L),
S	The dosage concentration
m	The mass of adsorbent
V	The initial volume of adsorbate solution
b_v	The breakthrough volume of the adsorbate (L).
ΔG	The standard free energy change
ΔH	The standard enthalpy change
ΔS	The standard entropy change
$\frac{dq}{dt}$	The rate of the uptake(mg/g)
k_1	The rate constant of pseudo first model (1/min).
q_t	Uptake the adsorbate with the change of time(mg/g),
k_2	The rate constant of the pseudo second order model, (g mg-1 min-1)
R	The gas constant (8.13 J/mol K)
T(K)	The absolute temperature
B	The constant gives the mean free energy
E	Free energy per molecule of the adsorbate
q_e	The adsorbate on the adsorbent (mg/g),
q_m	The maximum adsorption capacity of monolayer coverage (mg/g)
b	The constant related to the binding site (L/mg),
C_e	The concentration of molecule in the solution at equilibrium (mg /L).
K	The constant value
1/n	The constant for the intensity of the adsorption
K_d	The distribution coefficient (L/g).
D	The mean diameter the Scherer's' constant
θ	The Bragg angle
β	The width of peak at half height
λ	The X-Ray wavelength
K	The shape factor with value of about 0.9.

LIST OF ABBREVIATIONS

CTS/MMT	Chitosan/Montmorillonite
DBPs	Disinfection By-products
DDT	Dichlorodiphenyltrichloroethane
FTIR	Fourier Transform Infrared
FESEM	Field Emission Scanning Electron Microscopy
BET,(S_{BET})	Specific surface area by Brunauer-Emmett- Teller
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
MSN	Mesoporous Silica
NZVI	Nano Zero Valent Iron
NZVI/AL	Nano Zero Valent Iron supported on Alumina
NZVI/MSN	Nano Zero Valent Iron supported on Mesoporous silica
NZVI/SuAL	Nano Zero Valent Iron supported on carbon-coating alumina
NZVI/SuMSN	Nano Zero Valent Iron supported on carbon-coating Mesoporous silica
NZVI/SuZSM	Nano Zero Valent Iron supported on carbon-coating zeolite
NZVI/ZSM	Nano Zero Valent Iron supported on zeolite
HCB	Hex-chloric benzene
PCB	Poly chlorinated bi phenyl
PCDD/Fs	Polychlorinated di-benzoyl-dioxins and Di-benzoyl furans
POPs	Persistent Organic Pollutants
OCPs	Organic chlorine pesticides
TEM	Transmission Electron Microscopy
TCP	2,4,6-Trichlorophenol
$CHCl_3$	Trichloromethane/Chloroform
TGA	Thermal Gravimetric Analysis
US EPA	United States Environmental Protection Agency.
VOCs	Volatile organic compounds
ZSM-5	Zeolite Socony Mobil-5

PREPARATION AND CHARACTERIZATION OF SUPPORTED NANO-ZERO VALENT IRON FOR TREATMENT OF ORGANIC POLLUTANTS IN WATER

ATYAF KHALID HAMMED AL-DAHAN

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Doctor of Philosophy

Faculty of Industrial Sciences & Technology

UNIVERSITI MALAYSIA PAHANG

MAY 2017

ABSTRAK

Kehadiran bahan pencemar organik berbahaya dalam aliran air mengakibatkan masalah alam sekitar dan kesihatan. Oleh itu, kaedah penyingkiran yang berkesan adalah amat diperlukan. Salah satu kaedah penyingkiran yang berkesan serta ringkas dan murah adalah melalui proses penjerapan menggunakan bahan penjerap bersaiz nano seperti besi nano sifar valen (NZVI). Walau bagaimanapun, NZVI mempunyai beberapa kelemahan utama seperti kecenderungan untuk mengumpal serta kurang lasak yag menjejaskan kecekapan penjerapan. Oleh itu, NZVI tersokong telah diperkenalkan dan ditambahbaik melalui proses penyalutan lapisan karbon menggunakan D-glukosa sebagai sumber karbon yang baru. Ciri-ciri penjerap telah dikenalpasti menggunakan beberapa kaedah dan instrumentasi pencirian seperti XRD, FTIR, penjerapan gas N_2, TGA, FESEM-EDX dan TEM. Suhu dan keadaan dimana proses penyalutan karbon telah dikenalpasti memainkan peranan penting dalam menghasilkan lapisan karbon yang sekata serta mempunyai komposisi permukaan yang diperlukan bagi proses penjerapan yamg cekap. Dalam kes ini, suhu pada 500ºC adalah paling sesuai dan telah dibuktikan melalui nilai kecekapan penjerap serta hasil pencirian. Seterusnya, kajian lanjut kecekapan penjerap telah dibuat dengan menggunakan metilena biru (MB), 2, 4, 6-triklorofenol (TCP) dan kloroform ($CHCl_3$) dalam larutan akueus. Secara umum, penjerap bersalut karbon menghasilkan kapasiti penjerapan yang lebih tinggi. Parameter penjerapan telah dinilai (masa keseimbangan, 0-180 min; dos penjerap, 0.05-0.1g; kepekatan awal bahan jerapan, 10-40mg/L; suhu, 30-50ºC dan pH larutan, 2-9) untuk semua penjerap. Mekanisma proses jerapan telah ditentukan berdasarkan model isoterma Freundlich dan Langmuir dan didapati bahawa model Freundlich adalah sesuai untuk penjerapan MB. Nilai jerapan yang dibandingkan melalui q_{max} yang dikira melalui isoterma Langmuir bagi penjerap bersalut karbon adalah lebih tinggi dari penjerap yang tidak bersalut bagi semua jenis bahan jerapan yang telah diuji. Contoh yang jelas adalah bagi kes MB, penjerap bersalut karbon (NZVI/SuZSM) menunjukan kenaikan lebih dari 80% nilai q_{max} berbanding bahan yang tidak bersalut (NZVI/ZSM). Sifat sinergi diantara pertambahan permukaan teraktif serta kestabilan partikel NZVI dikenal pasti sebagai faktor utama yang bertanggungjawad keatas nilai q_{max} yang tinggi. Proses kinetik penjerapan itu juga digambarkan oleh model kinetik tertib-pertama dan kedua dan telah didapati bahawa model kinetik tertib kedua adalah terbaik untuk ketiga-tiga bahan jerapan yang diuji. Selain itu, kajian termodinamik juga telah dilaksanakan untuk menentukan tenaga bebas (ΔG^o), entalpi (ΔH^o) dan entropi (ΔS^o). Hasil kajian telah mendapati bahawa penjerapan $CHCl_3$ berlaku secara spontan manakala proses sebaliknya berlaku pada MB dan TCP. Secara umumnya, kajian ini telah berjaya menghasilkan bahan penjerap berasaskan NZVI tersokong serta disaluti lapisan karbon yang stabil serta berupaya menyingkirkan bahan jerapan dengan nilai q_{max} yang tinggi. Tambahan lagi, penjerap ini boleh dijana semula untuk proses penjerapan berikutnya tanpa kehilangan ketara kecekapan penjerapan.

ABSTRACT

The presence of hazardous organic pollutants in water stream creates the environmental and health problems. Thus, efficient removal approach is required. One of the relatively simple and cost effective approaches is through adsorption process in the presence of nano-adsorbent such as Nano Zero Valent Iron (NZVI). However, NZVI has several major restrictions such as agglomeration, low durability, and poor mechanical strength which would affect its adsorbent efficiency. In order to overcome these problems, supported Nano Zero Valent Iron (NZVI) has been introduced either on untreated or carbon-coated supporting materials. The preparation of carbon-coated supporting materials involved chemical functionalization via wet impregnation method by D-glucose as a carbon source followed by carbonization step at different temperature. The prepared adsorbents are characterized by XRD, FTIR, N_2-Physisorption, TGA, FESEM-EDX and TEM. It was found that the carbonization temperature is crucial for obtaining good coverage of carbon coating material and in this case, 500ºC is the optimum temperature. The feasibility of employing these nano-adsorbents in the removal of the three selected adsorbates (methylene blue (MB), 2, 4, 6-Trichlorophenol (TCP) and chloroform ($CHCl_3$) from aqueous solution is investigated in a series of batch experiments. In general, carbon-coated adsorbent produces higher adsorption capacity as compared to chemically modified adsorbents. The adsorption parameters (e.g. equilibrium time ranging between 0-180 min, the adsorbents dosage ranging between 0.05-0.1g, the initial concentration ranging between 10-40mg/L, the temperature ranging between 30-50ºC and the pH of solution ranging between 2-9) are established for all adsorbents. Then, the mechanism of the adsorption process is determined based on the Freundlich and Langmuir isotherm models and found that the Freundlich is a better fit with MB adsorption. The maximum adsorption uptakes (q_{max}) calculated by Langmuir isotherm model for carbon-coated adsorbent were found to be higher for all three tested adsorbates than those of uncoated supports adsorbents. For instance, in case of MB removal, 80% increment in q_{max} value was obtained for NZVI/SuZSM as compared to uncoated adsorbent counterpart. It is believed that the superior adsorption performance of carbon-coated adsorbent is due to the synergistic effect between the availability of functionalized active adsorption sites with porosity characteristics of supporting materials as well as the stability of NZVI nanoparticles. Besides, the kinetics of the adsorption process is well described by the pseudo-first and second order kinetics models and found the second order is the best fit for the three adsorbates on the all tested adsorbents. The thermodynamic studies for three adsorbates are performed to determine the free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) and found the spontaneity of $CHCl_3$ with negative value of (ΔG^o) onto all tested adsorbent, while non-spontaneity process at 30ºC with positive value of (ΔG^o) for adsorption of MB onto NZVI/ZSM and for TCP adsorption onto NZVI/MSN and NZVI/ZSM, respectively. In general, the current study confirms that the developed adsorbents are stable with high adsorption capacity as well as can be regenerated for subsequent adsorption process without appreciable loss of adsorption efficiency.

REFERENCES

Abdullah, A.H., Wooi, O.S., Kassim, A., Ahmad, F., Hussein, M. Z.Kuang, D. and Zainal, Z. 2001. Preparation and Characterization of Activated Carbon from Gelam Wood Bark (Melaleuca cajuput), Malaysian Journal of Analytical Sciences. 7(1): 65-68.

Abdel Ghafar, H. H., Fouad, O. A, Ali, G. A. M. and Makhlouf, S. A. 2013. Enhancement of adsorption efficiency of methylene blue on Co_3O_4/ SiO_2 nano composite. Journal of Desalination and Water Treatment. 53(11): 2980–2989.

Abd-El-Latif, M. M., El-Kadyl, M.F.and Ibrahim, A.M. 2010. Adsorption equilibrium, kinetic and thermodynamics of methylene blue from aqueous solutions using biopolymer of sawdust composite. Journal of American Science. 6(6):267-283.

Abrishamkar, M. and Izadi, A., 2013. Nano-ZSM-5 zeolite: Synthesis and application to electrocatalytic oxidation of ethanol. Journal of Microporous and Mesoporous Materials. 180:56–60.

Abrishamkar, M. and Kahkeshi, F. B. 2013. Synthesis and characterization of nano-ZSM-5 zeolite and its application for electro catalytic oxidation of formaldehyde over modified carbon paste electrode with ion exchanged synthesized zeolite in alkaline media. Journal of Microporous and Mesoporous Materials. 167: 51–54.

Adam, S. and Fakhri, A. 2013. Adsorption of 4-Chloro-2-Nitrophenol by zero valent iron nanoparticles and Pd-Doped zero valent iron nanoparticles surfaces: Isotherm, kinetic and mechanism modelling. Journal of Physical Chemistry and Biophysics.115: 2-9.

Agrawal, A. and Tratnyek, P.G.1996. Reduction of nitro aromatic compounds by zero valent iron metal. Journal of Environmental Science and Technology. 30:153–60.

Ahmad, R. and Kumar, R., 2010. Kinetic and thermodynamic studies of brilliant green adsorption onto carbon/iron oxide nano composite. Journal of the Korean Chemical Society, 2010, 54-61.

Aifiei, Y., Haoran, L., Yali, F., and Zhuwei, D. 2015. Mechanism of 2, 4, 6-Trichlorophenol degradation in microbial fuel cells system with microbe isolated from submarine sediment . International Journal of Electrochemical Science. 10: 1459 – 1468.

Ahi, H. and Shams, K. 2013. Synthesis of A zeolite nano crystals using kaolin via nano emulsion transonic technique and study of its sorption using a known kerosene cut. Journal of Microporous and Mesoporous Materials. 180 : 61–70.

Ahluwalia, S.S. and Goyal, D. 2005. Microbial and plant derived biomass for removal of heavy metals from wastewater. Journal of Bioresource Technology.98: 2243-2257.

Altare, C. R., Katz, L .E. Bowman, R. S., Sullivan, E. J. and Kinney, K. A. 2007. Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water. Microporous and Mesoporous Materials 105:305–316.

AL zaydien, A.S. 2009. Adsorption of methylene blue from aqueous solution onto a low-cost natural Jordanian Tripoli. American Journal of Applied Sciences. 6 (6): 1047–1058.

Allam, K., Bih, L., El-Bouari, A. and Belhorma, B. 2016. Removal of methylene blue from water using hydroxyapatite submitted to microwave irradiation. Journal of Water Resource and Protection.8: 358-371.

Ali, I., 2012. New generation adsorbents for water treatment. Journal of Chemical Reviews. 112 (10): 5073–5091.

Amuda, O.S., Olayiwol, A.O., Farombi, A.G., Alade, A. O. and Adebisi, S. A. 2014. Adsorption of methylene blue from aqueous solution using steam-activated carbon produced from Lantana camera Stem. Journal of Environmental Protection.5:1352-1363.

Ang, W.S., Lee, S. and Elimelech, M. 2006. Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes. Journal of Membrane Science.272: 198-210.

Arabi, S. and Mahmood Reza, S. 2014. Removal of methylene blue, a basic dye, from aqueous solution using nano zero valent iron. Journal of Water science and Technology. 70 (1):24-31.

Arivoli, S., Hema, M., Manju, N. and Parthasarathy, S. 2010. Adsorption dynamics of methyelen blue by acid activated carbon.Journal of Chemical and Pharmaceutical Research. 2(5):626-641.

Atkinson, J. D., Fortunato, M. E., Dastgheib, S. A., Rostam-Abadi, M., Rood, M. J., Suslick, K. S. 2014. Synthesis and characterization of iron-impregnated porous carbon spheres prepared by ultrasonic spray pyrolysis. Journal of Carbon.49:587-598.

Baciocchi, R., Boni, M.R.D. and Aprile, L. 2003. Characterization and performance of granular iron as reactive media for TCE degradation by permeable reactive barriers. Journal of Water Air Soil Pollution.149:211–226.

Badruddoza, A. Z. M., Uddin, M. S., Hazel, G. Si. Si. and Hidajat, K. 2010. Synthesis of carboxymethyl-β-cyclodextrin conjugated magnetic nano-adsorbent for removal of methylene blue. Journal of Colloids and Surfaces A: Physicochemical and Engineering Aspects. 367 (1-3): 85–95.

Ballesteros Martín, M. M., Sánchez Pérez, J.A., Casas López, J. L. and Malato, S.and Oller, I. 2010.A comparative study of different tests for biodegradability enhancement determination during AOP treatment of recalcitrant toxic aqueous solutions. Journal of Ecotoxicology and Environmental Safety.73:1189-1195.

Bandstra, J. Z., Tratnyek, P.G., Johnson, R.L. and Miehr, R. 2005. Reduction of 2, 4, 6-Trinitrotoluene by iron metal: kinetic controls on product distributions in batch experiments. Journal of Science Technology.39:230–238.

Bhattacharya, K.G.and Sarma, A. 2005. Kinetics and thermodynamics of methylene blue adsorption on neem (Azadirachta indica) leaf powder. Journal of Dyes Pigment. 65: 51-59.

Bhattarcharya, G.K. and Sarma, A. 2003. Adsorption characteristics of the dye, brilliant green on neem leaf powder. Journal of Dyes Pigment. 57: 211-222.

Bezbaruah, A.N., Krajangpan, S., Chisholm, B.J., Khan, E., Bermudez, J.J. 2009. Entrapment of iron nanoparticles in calcium alginate beads for groundwater remediation applications. Journal of Hazardous Materials. 166:1339–1343.

Bezbaruah, A.N., Khan, E., Shanbhogue, S. Sh, and Simsek, S. 2011. Encapsulation of iron nanoparticles in alginate biopolymer for Trichloroethylene remediation. Journal of Nanoparticle Research.13 (12): 6673–6681.

Bhatnagar, A. and Minocha, A. K . 2006. Conventional and non- conventional adsorbents for removal of pollutants from water-A review; Indian Journal of Chemical Technology IJCT. 13 (3):203-217.

Bowman, R. S. 2003. Applications of surfactant-modified zeolites to environmental remediation. Journal of Microporous and Mesoporous Materials. 61: 43–56.

Boehm F. 2009. Summary of the report: Nanotechnology in environmental applications: The Global Market, Report Code: NAN039B, July 2009, available at: http://www.bccresearch.com/.

Btatkeu, K., Caré, S., Noubactep, C. and Miyajima, K. 2013. Testing the suitability of metallic iron for environmental remediation. Discoloration of methylene blue in column studies. Chemical Engineering Journal. 215 (21): 959-968.

Bullough, F., SenGupta, A. K., Barrott, J., Coles, B. J., Weiss, D. J. and Dubbin, W. E. 2010. Evidence of competitive adsorption of Sb(III) and As(III) on activated alumina. Journal of Industrial Engineering and Chemistry Research. 49 (5): 2521–2524.

Bulut, Y. and Aydın, H. 2006. A Kinetics and thermodynamics study of methylene blue adsorption on Wheat Shells. Journal of Desalination. 194 (1-3): 259-267.

Campbell, N. A. and Mckay, R. J. 1982.Variable selection techniques in discriminant analysis II.Allocation. British Journal of Mathematical and Statistical Psychology. 35:30-4.

Canli, M., Bayca, S.U. and Abali, Y. 2013. Removal of methylene blue by natural and Ca and K-exchanged zeolite treated with hydrogen peroxide. Journal of Physicochemical Problems of Mineral Processing, 49 (2): 481–496.

Chandrasekhar, S. and Pramada, P.N. 2006. Rice husk ash as an adsorbent for methylene blue effect of washing temperature. Journal of Adsorption. 12 :27–43.

Chang, Ch., Zhu., L and Lian, F. 2011. Simultaneous adsorption and degradation of ɤ-HCH by n ZVI/Cu bimetallic nanoparticles with activated carbon support. Journal of Environmental Pollution. 159 (10): 2507-2514.

Changunda, K., Harris, M. and Deglon, D.A. 2008. Investigating the effect of energy input on flotation kinetics in an oscillating grid flotation cell. Journal of Minerals Engineering. 21: 924-929.

Chen, J. L., Li, Z. B., Ryan, J. A. and Al-Abed, S. R. 2001. Effects of pH on dechlorination of trichloroethylene by zero-valent iron. Journal of Hazardous Materials. 83 (3): 243-254.

Chen, G. Ch., Pignatellod, J. J., Shana, X. Q., Peia, Z. G., Wen, B., Liu, T., Xie, Y. N. and Wang, Y. Sh.2009. Adsorption of 2,4,6-Trichlorophenol by multi-walled carbon nanotubes as affected by Cu(II) .Journal of water research. 43: 2409-2418.

Cheng, I.F., Korte, N., Muftikian, R. and Fernando, Q.1997. Reduction of nitrate to ammonia by zero-valent iron. Journal of Chemosphere. 35: 2689–95.

Chung, H. K. , Park, J., Park, P. K., Cho, J., Kim, W. H. and Jeong, T. Y. 2015. Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent. Journal of Industrial and Engineering Chemistry. 28: 241–246.

Chiu, Y.C., Lu, C. J. and Chou, H.S. 2012. Interaction between zero-valent iron and hydrogen in anaerobic degradation of tetrachloroethylene. Journal of Sustainability Environmental Research. 22 (2):107-111.

Choi, Y. J. 2003. Critical flux, resistance and removal of contaminants in ultrafiltration (UF) of natural organic materials, M.Sc. University of Pennsylvania State.

Ci, L., Ruhle, M., Jin-Philipp, N. Y. and Ryu, Z. 2006. Investigation of the interfacial reaction between multi-walled carbon nanotubes and aluminium. Journal of Act Materials. 54: 5367-5375.

Cui, L., L., Yan, J., Li, L., Quan, G.,Ding, Ch.,Chen,T.,Yin,Ch.,Cao, J. 2015. Dose Biochar Alter the speciation of Cd and Pd in aqueous solution. Journal of Bio Resources 10 (1):88-104.

Costa, D. A. S., Mambrini, R.V., Moura, F. C. C., Macedo, W. A. A. and Fernandez-Outon, L. E. 2013. Magnetic adsorbent based on cobalt core nanoparticles coated with carbon filaments and nanotubes produced by chemical vapor deposition with ethanol. Chemical Engineering Journal 229 (1): 35–41.

Cundy, A. B., Whitby, R. L. D. and Hopkinson, L. 2008. Use of iron-based technologies in contaminated land and groundwater remediation: A review. Journal of Science of the Total Environment .400 (1-3):42-51.

Dada, A. O., Odebunmi, E. O. and Adekola, F. A. 2014. Synthesis and characterization of iron nanoparticles and its ash rice husk supported nano composite. Proceedings of the 1st African International Conference/Workshop on Applications, Nanotechnology to Energy, Health and Environment, UNN. 23-29:138-149.

Dakiky, M., Mereb, M., Khamis, M. and Manassra, A.2002. Selective adsorption of chromium VI in industrial wastewater using low-cost abundantly available adsorbents. Journal of Advances in Environmental Research. 6 (4):533-540.

De la Torre, A. I. R., Dominguez, J. M., Sandoval, G. , Torres Rodriguez, M. ,Ramos, C. E., Melo-Banda, J. A. and Angeles, R.C. 2010. Synthesis of hybrid (Ni-Mo) carbides/carbon-coated mesoporous materials and their catalytic properties for hydrocracking of intermediate paraffins (n-C8). Journal of Catalysis Today, 148 (1-2): 55–62.

Derakhshan, Z. and Baghapour, M.A., Faramarzian, M. and Ranjbar, M. 2013. Adsorption of methylene blue dye from aqueous solutions by modified Pumice Stone: Kinetics and equilibrium studies. Journal of Health Scope.2 (3):136-144.

Di Nezio, M. S., Pistonesi, M. F., Fragoso, W. D., Pontes, M. J.C., Goicoechea, H. C., Araujo, M. C. U. and Fernández Band, B. S. 2007. Successive projections algorithm improving the multivariate simultaneous direct spectrophotometric determination of five phenolic compounds in sea water. Journal of Microchemical 85: 194–200.

Dogan, M., Alkan, M. and Abak, H. 2008. Biosorption of methylene blue from aqueous solutions by hazelnut shells: Equilibrium, parameters and isotherms. Journal of Water Air and Soil Pollution. 192 (1): 141–153.

Elliott, D. W., Zhang, W. X. and Lien, H. L.2009.Degradation of lindane by zere – valent iron nanoparticles. Journal of Environmental Engineering. 5 (135): 317-324.

El-Toni, A.M.,Labis,J.P.Alhoshan,M.,Khan,A.andIbrahim,M.A.2013. Optimization of synthesis parameters for mesoporous shell formation on magnetic nanocores and their application as nanocarriers for Docetaxel Cancer Drug. International Journal of Mol. Sci. 14: 11496-11509.

El-Safty, Sh. A, Ismael, M. and Shahata, A. 2012. Mesoporous aluminosilica monoliths for the adsorptive removal of small organic pollutants. Journal of Hazardous Materials .201– 202: 23– 32.

EI-Rassy, H. and Al-Oweini.2009. Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si $(OR)_4$ and ROOSi $(ORO)_3$ precursors. Journal of molecular structure. 919 (1-3):140-145.

Estrada, A. L., Wang, A. and Li Y.Y. 2012. Biodegradability enhancement of wastewater containing cephalexin by means of the electro-Fenton oxidation process. Journal of Hazardous Materials. 227-228 : 41-48.

EI-Qada, N., Walker, G. M. and Allen, S. J. 2008.Adsorption of basic dyes from aqueous solution onto activated carbons, Chemical Engineering Journal.135 (3): 174-184.

Eshaghia, Z., Saeid Hussein, M. and Ebrahimib, M. 2011. Optimization of a novel method for determination of benzene, toluene, methylbenzene, and xylenes in hair and waste water samples by carbon nanotubes reinforced sol–gel based hollow fiber solid phase micro extraction and gas chromatography using factorial experimental design. Journal of Chromatography A, 1218 (21-27): 3400–3406.

Fang, L., Zhang, K.,Wu, P. and Chen, L..2013. Carbon coated mesoporous silica functionalized with sulfonic acid groups and its application to actualization. Chinese Journal of Catalysis, 34 (50) : 932–941.

Fan, J., Shi, Q., Zhang, J., Zhang, Ch., and Ren, L. 2011. Adsorption of 2, 4, 6-Trichlorophenol from aqueous solution onto activated carbon derived from loosestrife. Journal of Desalination. 267: 139–146.

Fatiha, M.and Belkacem, B. 2016. Adsorption of methylene blue from aqueous solutions using natural clay. Journal of Materials and Environmental Science.7 (1):285-292.

Fil, B.A., Korkmaz, M. and Özmetin, C. 2012. Cationic dye (methylene blue) removal from aqueous solution by montmorillonite. Journal of Bulletin of the Korean Chemical Society. 33 (10): .3184–3190.

Frost, R. L., He, H. and Xi, Y. 2010.Synthesis, characterization of palygorskite supported zero-valent iron and its application for methylene blue adsorption. Journal of Colloid and Interface Science. 341 (1): 153–161.

Fungaro, D., Borrelyb, S.I.,Izidoro, J.C.,Grosche, L.C. and Pinheiro, A.S. 2010. Adsorption of methylene blue from aqueous solution on zeolite material and the improvement as toxicity removal to living organisms. Orbital-The Electronic Journal for Chemistry. 2 (3): 235-247.

Geng, B., Li, T., Qi, X. and Jin, Z. 2009. Preparation of chitosan-stabilized Fe^0 nanoparticles for removal of hexavalent chromium in water. Journal Science of the Total Environment. 407: 4994-5000.

Gimba, C. E., Ocholi, O., Egwaikhide, P. A., Akporhonor, E. E. and Muyiwa, T.2009 New raw material for activated carbon. I. Methylene blue adsorption on activated carbon prepared from Khaya senegalensis fruits. Journal of Ciencia Investigation Agraria. 36 (1):107-114.

Gnanamoorthy, P., Ashok Prabu, V. and Karthikeyan, V. 2014. Field emission scanning electron microscopy (FESEM) characterization of the porous silica nanoparticulate structure of marine diatoms: Journal of Porous Materials. 21: 225–233.

Gouamid, M., Bensaci, M. B. and Ouahrani, M. R. 2013. Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using Date palm Leaves. Journal of Energy Procedia. 36: 898–907.

Gupta, V. K., Saleh, T. A. and Agarwal, Sh. 2011. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. Journal of Hazardous Materials. 185 (1): 17–23.

Gupta, V. K., Suhas, Carrott, P. J. M. and Ribeiro Carrott, M. M. L. 2009. Low- Cost adsorbents: Growing approach to wastewater treatment- a review. Journal of Critical Reviews in Environmental Science and Technology. 39 (10):783-842.

Gurses, A., Yalcin, M., Bayrak, R.,Dogar, C.,Karaca, S. and Acikyildiz, M. 2006. The adsorption kinetics of the cationic dye, methylene blue, onto clay. Journal of

Grassi, M., Kaykiogh, G., Belgiorn, V. and LofranoG. 2012. Removal of emerging contaminants from water and wastewater by adsorption process.Journal of Hazardous Materials.131 (1-3): 217–228.

Hameed, B.H., Latiff, K.N. and Ahmad, L. 2007. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Journal of Dyes and Pigments, 75(1):143–149.

Hameed, B.H. 2009a. Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. Journal of Hazardous Materials. 162:344–350.

Hameed, B.H. 2009b. 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.

Hajira, T., Mohammed, S. and Qazi, J. 2008. Removal of basic dye methylene blue by using bio absorbents Ulva Lactuca and Sargassum. African Journal of Biotechnology. 7 (15):2649-2655.

Hamdaouia, O. and Naffrechoux, E. 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. Journal of Hazardous Materials. 147 : 381–394.

Han, Y.Ch. Heo, J.K., Kim, Y.H., Kang, Y.S.and Kang, Y.Ch. 2006. A magnetic behaviour of alpha Fe nanopartical. .Department of Chemistry, Pukyong National University, 599-1 Daeyeon-3-dong, Nam-gu, Busan 608-737.

He, F. and Zhao, D. 2005. Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. Journal of Environmental Science and Technology.39: 3314–20.

He, F. and Zhao, D. 2007. Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers. Journal of Environmetal Science and Technology. 41:6216–21.

He, F., Roberts, C.B., Zhao, D. and Liu, J. 2007. Stabilization of Fe–Pd nanoparticles with sodium carboxyl methyl cellulose for enhanced transport and DE chlorination of Trichloroethylene in soil and groundwater. Journal of Industrial Engineering and. Chemistry Research. 46:.29–34.

He, F., Zhao, D. and Paul, C. 2010. Field assessment of carboxyl methyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. Journal of Water Research. 44 :2360–2370.

Hernandez, M. A., Rojas, F.and Corona, L. 2000. Adsorption characteristics of natural erionite, clipnotilolite and mordenite zeolites from Mexico. Journal of Adsorption. 6 (1): 33–45.

Ho, K., Y., Yeung, K. L., and Mckay, G. 2003. Selective adsorbents from ordered mesoporous silica. Langmuir. 19 (7): 3019-3024.

Ho, Y., Sulochana, N. and Malarvizhi, R. 2009. Equilibrium isotherm studies of methylene blue adsorption onto activated carbon prepared from Delonix regia Pods. Journal of Environmental Protection Science. 3: 111–116.

Hojabri, A., Soltanpoor, N., Hedayati, F. and Hajakbari, F. 2014. Annealing temperature effect on the properties of untreated and treated copper films with oxygen plasma. Journal of Theoretical of Applied Physics. 8:132-137.

Hoshikawa, Y., Kyotani, T., Komiyam, H., Castro-Muniz, A., Nanbu, H., Yokoyam, T., and Ishli, T. 2014. Remarkable enhancement of pyrolytic carbon deposition on ordered mesoporous silicas by their trimethylsilylation. Journal of Carbon. 67:156–167.

Hussein, S., Choong, Y., Khan, M. A., Malekbala, M. R., Thomas, S. and Cheah, W. 2011. Carbon coated monolith, a mesoporous material for the removal of methyl orange from aqueous phase: Adsorption and desorption studies. Chemical Engineering Journal. 171(3): 1124–1131.

Huirache-Acuna, R., Alonso-Nuez, G., Nava, R., Lara-Romero, J., Peza-Ledesma, C. L., Rivera-Munoz, E. M. and Pawelec, B. 2013. SBA-15 Mesoporous silica as catalytic support for hydride sulfurization catalysis-review. Journal of Materials. 6 (9):4139-4167.

Huh, Y., Lee, C. J., Lee, J. Y., Lee, T. J., Cheon, J. , Hong, Y. K. and Koo, J. Y. 2003.Controlled growth of carbon nanotubes over cobalt nanoparticles by thermal chemical vapor deposition. Journal of Materials Chemistry. 13: 2297–2300.

Hundal, L. S ., Powers, W.L. Comfort, S. D., Shea, P.J. Singh, J. and Bier,E.L.1997.Removal of TNT and RDX from water and soil using iron metal. Journal of Environment and Pollution. 97: 55–64.

Hwang, Y. H., Shin, H. S., and Kim, D. G. 2011. Mechanism study of nitrate reduction by nano zero valent iron; Journal of Hazardous Materials.185 (1-3) :1513–1521.

Idris, A., Bakar, I., Abdul Razak, P. R., Mohd Zin, H., Ibrahim, Z., Hashim,R., Ahmad,W. A. and Abdul Rahman, R .2007. Application of bioremediation process for textile wastewater treatment using pilot plant. International Journal of Engineering. 4 (2):228–234.

Inbaraj, J. J., Chignell, C. F. and Bilski, P. 2002. Photo physical and photochemical/studies of 2-Phenylbenzimidazole and UVB sunscreen 2-Phenylbenzimidazole-5-sulfonicacids, Journal of Photochemistry and Photobiology.75 (2):107-116.

Insa, S., Salvado, V. and Antico, E. 2006. Assays on the simultaneous determination and elimination of chloroanisoles and chlorophenols from contaminated cork samples. Journal of Chromatography A. 1122 (1-2): 215-221.

Ishihara, A., Nasu, H. and Hashimoto, T. 2012. Large mesopores generation in an amorphous silica-alumina by controlling the pore size with the gel skeletal reinforcement and its application to catalytic cracking. Catalysts Journal. 2: 368-385.

Itoh, T., Hoshikawa, Y., Shun-ichi, M., Mizuguchi, J., Arafune, H. and Hanaoka, T.2012. Production of l-the amine using glutamines encapsulated in carbon-coated mesoporous silica with high pH stability.Bio-Cheimal Engineering Journal.68 (15):207-214.

Jafari-zare, F. and Habibi-yangjeh, A. 2010. Competitive adsorption of methylene blue and rhodamine B on natural zeolite: Thermodynamic and kinetic studies. Chinese Journal of Chemistry.28:.349–356.

Jaafar, N.F., Asaan, H., Muhd Muhid, M. N., Abdul Jalil, A., Sapawe, N., Satar, M. A. H. and Triwahyonoa, S. 2012. Photodecolorization of methyl orange over -Fe_2O_3-supported HY catalysts: The effects of catalyst preparation and dealumination: Chemical Engineering Journal. 191 : 112– 122.

Jeyanthi, J. and Dhinakaran, M. 2012. Study of the removal of methylene blue from aqueous solution by using coir pith. Journal of Experimental Sciences 3(9) : 21-26.

Jin, X., Chen, Z., Pei, Z., Shan, X. and Jiang, M. 2008. Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite. Journal of Colloid and Interface Science. 328 (2) : 243–247.

Juang, L. Ch., Wang, Ch. C.,Hsu, T. Ch. and Lee, Ch. K. 2007. Dyes adsorption onto organoclay and MCM-41. Journal of Environmental Engineering Management 17(1):29-38.

Kadirova, Z. C., Okada , K., Katsumata, K., Isobe, T. , Matsushita, N. and Nakajima, A. 2013. Adsorption and photodegradation of methylene blue by iron oxide impregnated on granular activated carbons in an oxalate solution. Journal of Applied Surface Science. 284:72-79.

Kahani, S. A., Vadadi, O. and Hamadanian, M. 2007. Deposition of magnetite nanoparticles in activated carbons and preparation of magnetic activated carbons. Journal of Nanotechnology and Its Applications, First Sharjah International Conference: 183-188.

Kakavandi, B., Kalantary, R. R., Jafari, A. J., Nasseri, S., Esrafily, A. and Ameri, A. 2013. Synthesis and properties of Fe3O4-activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies. Iranian Journal of Environmental Health Science and Engineering.10 (1):10-19.

Kareem, S.H., Jalhoom, M.G. and Ali, I.H. 2014. Synthesis and characterization of organic functionalized mesoporous silica and evaluate their adsorptive behavior for removal of methylene blue from aqueous solution. American Journal of Environmental Sciences, 10(1):48–60.

Kareem , S. H., Jalhoom, M.Q. and Alib, I.H. 2015. Kinetic and thermodynamic study of Triton x-100 removal from aqueous solution of functionalized mesoporous silica. International Journal of Sciences :Basic and Applied Research (IJSBAR). 21(2): 293-308.

Kamikura, S., Yoshida, Y., Uchida, T., Naka, K., Asaji, T. and Uchiyama, H. 2011. Single walled carbon nanotube growth using cobalt nanoparticles prepared by vacuum deposition on a surface-active liquid. Journal of Diamond and Related Materials. 20 (7): 863–865.

Kanel, S. R., Greneche, J. M. and Choi, H. 2006. Arsenic (V) removal from groundwater using nano scale zerovalent iron as a colloidal reactive barrier material. Journal of Environmental Science and Technology.40: 2045–2050.

Kannan, N. and Sundaram, M. M. 2001. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. Journal of Dyes and Pigments 51 (1) : 25–40.

Khannan, P. K., Marimuthu, R.S., Adhyapak, P. V., Singh, N.and Gaikwad, S. 2007. Synthesis and characterization of copper nanoparticles. Journal of Materials Letters. 61: 4711–4714.

Kirsanov, M.P. and Shishkin, V.V. 2016. Evaluation and improving the efficiency of the use of activated carbon for the extraction of organo chlorine compound in water technology. Foods and Raw Materials. 4(1):148-153.

Kim, S. A., Oh, B. T., Kannan, S. K., Kim, H. M., Lee, W. H., Lee, K. J., Shea, P. J. and Park, Y. J. 2013. Removal of Pb (II) from aqueous solution by a zeolite–nanoscale zero-valent iron composite. Chemical Engineering Journal. 217 : 54–60.

Krishnaiah, D., Sarbatly, R., Anisuzzaman, S. M. and Bono, A. 2013. Adsorption of 2, 4, 6-Trichlorophenol (TCP) onto activated carbon. Journal of King Saud University.25 (3):251-255.

Kubuki, Sh., Nishida, T., Shibano, K., Homonnay, Z., Akiyama, K. and Kuzmann, E.. 2012. Decomposition mechanism of methylene blue caused by metallic iron-maghemite mixture. Journal of Hyperfin Interaction. 218 (1):47-13.

Kulkarni, S. J. and Kaware, J. P. 2015.Phenol desorption from adsorbent-A review. International Journal of Engineering Sciences & Management Research.2 (6): 6 - 8.

Kumar, P.R., Khilar, K.C., Mahajan, S.P. and Chaudhari, S. 2004. Removal of arsenic from water by electrocoagulation. Journal of Chemosphere. 55: 1245-1252.

Kushwaha, A. K., Chattopadhyaya, M.C. and Gupta, N. 2014. Enhanced adsorption of methylene blue on modified silica gel: equilibrium, kinetic, and thermodynamic studies. Journal of Desalination and Water Treatment. 52 (22-24): 4527-4537.

Kyzas, G.Z.,Matis,K.A. and Fu, J. 2013. The change from past to future for adsorbent materials in treatment of dyeing wastewaters. Journal of Materials, 6: 5131-5158.

Kwon, T., Kyotani, T., Setoyama, N., Fukushima, Y., Fukura, Y., Nishihara, H. and Inde, K. 2010. Carbon-coated mesoporous silica as an electrode material. Journal of Microporous and Mesoporous Materials.132 (3):421–427.

Lata, H., Gupta, R. K. and Garg, V. K. 2007. Removal of a basic dye from aqueous solution by adsorption using Parthenium hysterophorus: An agricultural waste. Journal of Dyes Pigments. 74: 653-658.

Lavand, A. B. and Malghe, Y. S. 2015. Nano sized C doped TiO_2 as a visible light photocatalyst for the degradation of 2, 4, 6- Trichlorophenol. Journal of Advance Materials Letters. 6 (8): 695-700.

Lee, Ch. L., Wang, H. P. and Jou, Ch. J. 2010. Enhanced degradation of chlorobenzene in aqueous solution using microwave-induced zero-valent iron and copper particles. Journal of Water Environment Research. 82(7): 642-647.

Leo, P., Calleja,G., Oracjo,G., Briones, D., Wojtas, L. and Martínez, F. 2016. New URJC-1 material with remarkable stability and acid-base catalytic properties.Polymer.8 (44):2-12.

Lepot, N., Mullens, J.,Van Bael,M.K., Haen, J. D., Franco,D.,Van den Rul, H. and Peeters, R. 2008. Synthesis of platelet-shaped boehmite and ɤ-alumina nanoparticles via an aqueous route. Ceramics International.34:1971–1974.

Lakher,S. K.,Shuman,S. and Sreeharsh,A.2015.Synthesis and characterization of 13X Zeolite/ Activated carbon composite. International Journal of Chemtech Research 7(3): 1364-1368.

Liang, S., Guo, X., Feng, N., and Tian, Q. 2009. Application of orange peel xanthate for the adsorption of Pb+2 from aqueous solutions. Journal of Hazardous Materials. 170 (1): 425-429.

Ling, X., Li, J., Zhu, W., Zho, Y., Shen, J., Sun, X., Han, W., Jiangsu, L.W. 2012. Synthesis of nanoscale zero-valent iron/ordered mesoporous carbon for adsorption and synergistic reduction of nitrobenzene. Journal of Chemosphere .87(6): 655-660.

Lin, C. J. and Lo, S. L. 2005. Effects of iron surface pretreatment on sorption and reduction kinetics of trichloroethylene in a closed batch system. Journal of Water Research. 39(6): 1037-1046.

Li, L., van, L., Fan, M. and Brown, R.C. 2006. Synthesis, properties, and environmental applications of nano scale iron-based materials-A review. Journal of Critical Reviews in Environmental Science and Technology.36: 405–431.

Li , X. Q. and Zhang, W. X. 2007. Sequestration of metal cations with zerovalent iron nanoparticles – a study with high resolution X-ray photoelectron spectroscopy (HR-XPS). Journal of Physical Chemistry. 111 (17):6939–6946.

Li, Z. Ch.,Hou, J.,Zeng, Ch., Yang, J., Li, Z.,Wu,., P.,Zhai, X.,Zhang,W., Fan,X. and Wang,Ch. 2011. Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources. Journal of ACS Nano. 5 (4): 3385-3390.

Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S., Lowry, G.V. 2005. TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Journal of Environmental Science and Technology .39:1338–45.

Lin, C. C., Kuo, C. T., Pan, F. M., Chang, K. C. and Kuo, C. T. 2009.Mechanistic study of cobalt catalyzed growth of carbon nanofibers in a confined space by plasma-assisted chemical vapour deposition. Journal of Diamond and Related Materials. 18 (10):1301–1305.

Mambrini, R. V., Moura, F. C. C., Fonseca, T. L., Dias, A., Oliveira, L.C.A. and Araujo, M.H. 2012. Magnetic composites based on metallic nickel and molybdenum carbide: a potential material for pollutants removal. Journal of Hazardous Materials. 241–242 : 73–81.

Mansoori, G. A., Bastami, A., Rohani, T., Eshaghi, Z. and Ahmadpour, A.2008. Environmental application of nanotechnology. Annual Review of Nano Research. (2).chap.2:1-75.

Maezawa, A., Suzuki, Y., Uchida, S., Suzuki, K., Furusawa, K. T. and Nakadoi, H.2007. Treatment of dye wastewater by using photo-catalytic oxidation with sonication. Journal of Ultrasonic Sonochemistry. 14: 615–620.

Miao, C.,Zheng, Ch., Xie, Y.and Liang,O. 2011. Chemical vapor deposition of Graphene,physics and applications of Graphene - experiments, Dr. Sergey Mikhailov (Ed.), ISBN: 978-953-307-217-3.

Malekbala, M. R. , Hussein, S., Abdullah, L. Ch., Choong, Th. S. Y. and Khan, M. A. 2015. Adsorption/desorption of cationic dye on surfactant modified mesoporous carbon coated monolith: Equilibrium, kinetic and thermodynamic studies. Journal of Industrial and Engineering Chemistry. 21: 369–377.

Metcalf and Eddy 2003. (4th ed). Wastewater engineering – treatment and reuse. New York. United States (US). McGraw-Hill Companies.

Mansourpanah, Y., Taheri, A. H. , Rahimpour, A., Farhadian, A.and Madaeni, S. S. 2009. Formation of appropiate sites on nano filtration membrane surface for binding TiO_2 photo-catalyst: Performance, characterization and fouling-resistant capability. Journal of Membrane Science. 330(1-2): 297-306.

Matus, V., Gonzalez , B., Martinez, M., and Sanchez, M. A. 2003. Efficient degradation of 2,4,6-Trichlorophenol requires a set of catabolic genes related to TCP genes from ralstonia eutropha JMP134(pJP4). Journal of Applied and Environmental Microbiology.69 (12): 7108–7115.

Merzougui, Z. and Addoun, F.2008. Effect of oxidant treatment of date pits activated carbons application to the treatment of waters. Desalination Journal. 222:394-403.

Mohan, D. and Singh, K. P. 2002. Single –and multi component adsorption of cadmium and zinc using activatrd carbon derived from bagasse-an agricultural. Journal of Water Research. 36 (9) : 2304-2318.

Molinari, R., Schiavello, M., Mungari, M., Palmisano L., Drioli, E., Di Paola, A. and Loddo, V. 2000. Study on a photocatalytic membrane reactor for water purification. Journal of Catalysis Today. 55(1-2) : 71-78.

Moraci, N. and Calabro, P. S. 2010. Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers. Journal of Environmental Management. 91(11):2336-2341.

Moni, L., Marra, A..,Acquarica, I. D.,Gasparrini, F.,Ciogli, A. and Dondoni, A.2010.Synthesis of sugar-based silica gels by copper- catalyzed Azido-activted silica intermediate and the use of gels in hydrophilic interaction chromatography. Chemistry: A European Journal. 16: 5712 – 5722.

Morshedi, D., Mashhadi, M., Boojar, A., Mohammadi, Z. and Akbari, A. 2013. Using protein nano fibrils to remove azo dyes from aqueous solution by the coagulation process. Journal of Colloids and Surfaces B: Bio.inter. faces. 112: 245-254.

Muhaisn F. M., 2014. Competitive removal of heavy metal ions from simulated wastewater by sportive flotation using Punica Granatum. MsC thesis, University of Baghdad.

Muslim, M., A. and Hammoud, Z., A. 2014. Removal of methylene blue from aqueous solution by using iron filings waste material in batch and continuous experiments. Journal of Babylon University/Engineering Sciences.22 (1):35-45.

Naddafi, K., Nabizadeh, R., Sarkhosh, M., Gholami, M., Saeedi, R. and Rastkari, N. 2016. Adsorption of 2, 4, 6-Tricholophenol from aqueous solutions by a surfactant-modified zeolitic tuff: Batch and continuous studies. Journal of Desalination and Water Treatment. 57 (13): 5789-5799.

Nagata, H., Nakahira, A., Takimura, M. and Yamasaki, Y. 2006. Syntheses and characterization of bulky mesoporous silica MCM-41 by hydrothermal Hot-Pressing method. Journal of Materials Transactions. 47 (8): 2103 -2105.

Nebagha, K.,C., Zita,K.,Rghiouib,L.,Khayetd,M.,Saidi,M. and Najif, A. 2015. Adsorptive removal of copper(II) from aqueous solutions using low cost Moroccan adsorbent. Part II: Kinetic and equilibrium studies .Journal of Materials Environmental Sciences. 6 (10): 2694-2702.

Noubactep, C., Caren, R. and Care, S. 2012. Nano scale metallic iron for environmental remediation: prospects and limitations. Journal of Water Air Soil Pollution. 223 (3) :1363–1382.

Nikolaidis, N. P., Lackovic, J. A. and Dobbs, G. M. 2003. Arsenic removal by zero-valent iron: field, laboratory and modeling studies. Journal of Water Research. 37:1417–1425.

Nishihara, H., Kwon, T., Fukura, Y., Iwamura, S., Hoshikawa, Y. and Nakayama, W. 2011. Fabrication of a highly conductive ordered porous electrode by carbon-coating of a continuous mesoporous silica film. Journal of Chemistry of Materials. 23 (13): 3144–3151.

Nurmi, J. T., Tratnyek, P. G., Baer, D. R., Amonette, J. E., Penn, R. L., Driessen, M. D., Linehan, J. C., Matson, D.W., Pecher, K., Wang, C. and Sarathy, V. 2005. Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry and kinetics. Journal of Environmental Science and Technology. 39(5):1221-1230.

O'Carroll, D., Kocur, Ch., Boparaia, H., Krola, M. and Sleep, B. 2013. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Journal of Advances in Water Resources. 51:104-122.

Oh, S. Y., Kim, B. J., Cha, D. K. and Chiu, P. C. 2006. Enhanced reduction of perchlorate by elemental iron at elevated temperatures. Journal of Hazardous Materials. 129(1-3): 304-307.

Oyelude, E .O. and Appiah-Takyi, F. 2012. Removal of methylene blue from aqueous solution using alkali-modified malted sorghum mash. Turkish Journal of Engineering and Environmental Sciences. 36 (2):161–169.

Ozdemir, F. A., Apak, R. and Demirata, B. 2009. Adsorptive removal of methylene blue from simulated dyeing wastewater with melamine-formaldehyde-urea resin. Journal of Applied Polymer Science. 112(6): 3442–3448.

Okewale, A.O., Olalekan, A.P and Babayemi, K.A. 2013. Adsorption isotherm and kinetics models of starchy adsorbents on uptake of water from ethanol water system. International Journal of Applied Science and Technology.3 (1):35-42.

Patil, B. S. and Kulkarni, K. S. 2012. Development of high surface area activated carbon from waste materials. International Journal of Advanced Engineering Research and Studies, IJAERS.1 (11):109-113.

Petala, E., Karakassides, M. A., Dimos, K., Zboril, R., Douvalis, A., Tucek, J. and Bakas, T. 2013. Nano scale zero-valent iron supported on mesoporous silica: Characterization and reactivity for Cr(VI) removal from aqueous solution . Journal of Hazardous Materials.216 (2): 295-306.

Phenrat, T., Lowry, G., Saleh, N., Sirk, K., Tilton, R. and Kim, H. J. 2008. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. Journal of Nanopartical Research.10:795–814.

Ponder, Sh. M., Darab, J. G., Bucher, J., Craig, L., Davis, L., Caulder, D., Lukens, W., Rao, L., Edelstein, N., Mallouk, TH. E., Shuh, D. K. and Nitsche, H.2001.Surface chemistry and electrochemistry of supported zero valent iron nanoparticles in the remediation of aqueous metal contaminants. Journal of Chemical Materials. 13:479-486.

Pourahmad, A. and Sohrabnezhad, Sh. 2010. Comparison absorption of new methylene blue dye in zeolite and nanocrystal zeolite. Journal of Desalination. 256 (1-3): 84–89.

Prema, P., and Selvarani, M. 2013. Evaluation of antibacterial efficacy of chemically synthesized copper and zero valent iron nanoparticles. Asian Journal of Pharmaceutical and Clinical Research. 6 (3): 223-227.

Puranik, P., Paknikar, K. and Modak, J. 2005. A comparative study of the mass transfer kinetics of metal bio sorption by microbial biomass. Journal of Hydrometallurgy.52 (2):189–197.

Qiu, X., Xu, Z., Lianga, B., Fang, Z. and Gu, F. 2011. Degradation of decabromodiphenyl ether by nano zero-valent iron immobilized in mesoporous silica microspheres. Journal of Hazardous Materials.193:70–81.

Qu, X., Li, Q., Alvarez, J. and Pedro, J. 2013. Applications of nanotechnology in water and wastewater treatment. Journal of Water Research.47:3931-3946.

Raghu, S. and Basha, C. A . 2007. Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater. Journal of Hazardous Materials. 149 : 324–330.

Rahman, M. A., Alam, A. M. S. and Amin, S. M. R. 2012. Removal of methylene blue from waste water using activated carbon prepared from Rice Husk. Dhaka University Journal of Science.60 (2):185–189.

Rajeshwar, M. Sh., Rami, R. P., Bhadra,P. P., and Amar, P.Y. 2012. Preparation and characterization of activated carbon from Lapsi (Choerospondias axillaris) Seed Stone by Chemical Activation with Phosphoric acid. Research Journal of Chemical Science.2 (10): 80-86.

Ramos, R. L., Berber-Mendoza, M. S., Jacobo-Azuara, A., Guerrero-Coronado, R. M. and Diaz-Flores, P. E. 2008. Adsorption of chromium (VI) from an aqueous solution on a surfactant- modified zeolite. Journal of Colloids and surface A: Physico.Chem.Eng.Aspects. 330 (1) : 35-41.

Rios, R. V. R. A. ,Escribano, J. A.,Sabio, M.M.,Reinoso, R. F. and Albero, S.J. 2007. Kinetic restrictions in the characterization of narrow micro porosity in carbon Materials. Journal of Physical Chemistry. 111: 3803-3805.

Sayles, G. D., You, G. R., Kupferle, M. J. and Wang, M. X.1997. DDT, DDD, and DDE Dechlorination by zero-valent iron. Journal of Environmental Science and Technology.31:3448-3454.

Sakulchaicharoen, N., Herrera, J. E. and O'Carroll D.M. 2010. Enhanced stability and dechlorination activity of pre-synthesis stabilized nanoscale FePd particles. Journal of Contam Hydro . 118 (3-4) :117–27.

Salavati-Niasari, M. and Davar, F. 2009. Synthesis of copper and copper(I) oxide nanoparticles by thermal decomposition of a new precursor. Journal of Materials Letters. 63 (3-4): 441–443.

Saleh, N., Lowry, G.V., Matyjaszewski, K., Tilton, R. D., Sirk, K., Dufour, B.,Liu, Y., and Phenrat, T. 2007. Surface Modifications Enhance Nanoiron Transport and NAPL Targeting in Saturated Porous Media. Journal of Environmental Engineering and Science.24 (1):45-57.

Saleh, N., kim, J. H., Lowry, G., Matyjaszeweki, K., Tilton, R. and Phenrat, T. 2008. Ionic strength and composition affect the mobility of surface-modified Fe^{o} nanoparticles in water-saturated sand columns. Journal of Environmental Science and Technology. 42: 3349–3355.

Satapanajaru, T., Park, J., Anurakpongsatorn, P., Songsasen, A. and Boparai, H. 2006. Low-cost iron byproducts from automotive manufacturing to remediate DDT. Journal of Water Air Soil Pollution.175:361–374.

Sarioglu, M. and Atay, U. 2006. Removal of methylene blue by using biosolid. Global NEST Journal.8 (2): 113–120.

Senzaki, T.and Kumagai,T. 1989. Removal of chlorinated organic compounds from wastewater by reduction process: treatment of trichloroethylene with iron powder. Kogyo Yosui . 369:19–25.

Sergiienko, R., Qin, G. W., Shibata, E., Zentaro, A., Nakamura, T. and Shindo, D. 2007. Formation and characterization of graphite-encapsulated cobalt nanoparticles synthesized by electric discharge in an ultrasonic cavitation field of liquid ethanol. Journal of Act Materially. 55 (11) : 3671–3680.

Schrick, B., Mallouk, Th. E., Hydutsky, B. W and Blough, J. L. 2004. Delivery vehicles for zero valent metal nanoparticles in soil and ground water. Journal of Chemistry and Materials. 16: 2187-2193.

Shah, I., Alappat, B.J. and Pre, P.2013.Steam regeneration of adsorbents: An experimental and technical review. Chemical Science Transactions. 2 (4):1078-1088.

Shaibu, S. E., Adekola, F. A, Ayanda, O. S. and Adegoke, H. I. 2014. A Comparative study of the adsorption of methylene blue onto synthesized nanoscale zero-valent iron-bamboo and manganese-bamboo composites. Journal of Materials.7(6): 4493-4507.

Sharker, M. and Acharya, P.K. 2006. Use of the fly ash for the removal of phenol and its analogues from contaminated water. Journal of Waste Management. 26 (6): 559-570.

Shahryari, Z., Goharrizi, A., S., and Azadi, M. 2010. Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. International Journal of Water Resources and Environmental Engineering, 2(2): 016-028.

Shams, K. and Ahi, H. 2013. Synthesis of 5A zeolite nanocrystals using kaolin via nano emulsion ultrasonic technique and study of its sorption using a known kerosene cut. Journal of Microporous and Mesoporous Materials. 180 : 61–70.

Shehata, A. M. A. 2013. Removal of methylene blue dye from aqueous solutions by using treated animal bone As A cheap natural adsorbent. International Journal of Emerging Technology and Advanced Engineering. 3(12) : 507–513.

Shih, Y.H. and Tai, Y.T. 2010. Reaction of decabrominated diphenyl ether by zerovalent iron nanoparticles. Journal of Chemosphere. 78(10) :1200–1206.

Shiue, A., Chang, Ch. T., Ma, Ch. M. and Ruan, R. T. 2012. Adsorption kinetics and isotherms for the removal methyl orange from wastewaters using copper oxide catalyst prepared by the waste printed circuit board Sustain. Journal of Environmental Science Research. 22 (4): 209-215.

Shih, Y. H., Tso, C. P. and Tung, L. Y. 2010. Rapid degradation of methyl orange with Nano scale zero valet iron particles. Journal of Environmental Engineering Management. 20 (3): 137-143.

Shi, L., Chen, K., Du, R., Bachmatiuk, A., Rummeli, M. K., Xie, K.,Zhang,Y.,Liu,Z.and Huang,Y. 2016. Scalable seashell-based chemical vapour deposition growth of three –dimensional Graphene foams for oil-water separation. Journal.American. Chemical Society.138: 6360−6363.

Shukla, P. R., Tade, M. O., Wang, Sh. and Ang., H.M. 2009. Synthesis, characterisation, and adsorption evaluation of carbon-natural-zeolite composites. Journal of Advanced Powder Technology. 20 (3): 245–250.

Signorini, L., Bonetti, E., Pasquini, L., Savini, L., Boscherini, F. and Carboni, R. 2003. Size dependent oxidation in iron/iron oxide core-shell nanoparticles. Journal of Physical Review B. 68 (19):195423-195431

Silva, G. C., Ciminelli, V.S., Lopez, J. L., Ferreira, A. M., Paiva, P. R. and Pissolati, N. C. 2014. A facile synthesis of Mn_3O_4/Fe_3O_4 super paramagnetic nano composites by chemical precipitation: Characterization and application in dye degradation. Journal of Materials Research Bulletin.49: 544–551.

Siskova, K.M., Tucek, J., Zboril, R., Krizek, M., Machala, L.and Straska, J. 2013. Formation of zero-valent iron nanoparticles mediated by amino acids.International Symposium on Environmental Science and Technology. Procedia Environmental Sciences 18:809-817.

Singh, D.K and Srivastava, B. 2002. Removal of phenol pollutants from aqueous solution using various adsorbents .Journal of Scientific and Industrial Research.61:208-218.

Su, C. M. and, Puls, R.W.2001. Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for *in situ* groundwater remediation. Journal of Environmental Science and Technology. 35:1487–1492

Sun, Y. P., Wang, H.P., Zhang, W.X. and Cao, J. S. 2006. Characterization of zero-valent iron nanoparticles. Journal of Advance in Colloid and Interface science.120 (1-3):47–56.

Sun, Y. P., Wang, H.P., Zhang, W.X. and Li, X. Q. 2007. A method for the preparation of stable dispersion of zero-valent iron nanoparticles. Journal of Colloid Surface A .308 (1-3) : 60–66.

Sun, X., Wang, L., Yan, Y., Li, J. and Han, W. 2014. SAB-15-incorporated nanoscale zero-valent iron particles for chromium(VI) removal from groundwater: Mechanism, effect of pH, humic acid and sustained reactivity. Journal of Hazardous Materials. 12: 26-33.

Sundrarajan, M., Joseph, K. and Vishnu, G. 2007. Ozonation of light-shaded exhausted reactive dye bath for reuse. Journal of Dyes Pigments. 75 :273–278.

Suteu, D., Malutan, T. 2013. Industrial Cello lignin wastes as adsorbent for removal of methylene blue dye from aqueous solutions. Journal of Bio Resources. 8(1):427-446.

Tahir, N, M., Ariffin, M. M., Khoon, T. S., Hui, T. J. and Suratman, S. 2008. Adsorption of chloroformethyl and metsulfuron-methyl on selected Selangor agricultural soils, The Malaysian Journal of Analytical Sciences.12 (2):341-347.

Tan, I. W., Hameed, B. H. and Ahmad, L. 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. Journal of Hazardous Materials.154 (1-3):.337–346.

Tan, I. A. W., Hameed, B. H. and Ahmad, A. L. 2009. Adsorption isotherms, Kinetics, thermodynamics and desorption studies of 2, 4, 6-Trichlorophenol on Oil Palm Empty Fruit Bunch-based activated carbon. Journal of Hazardous Materials. 164 (2-3):473-482.

Tang, L., Xiong, W., Tang, J., Zeng, G., Wang, J., Xie, X., Fang, Y., Zhou, Y., Pang, Y. and Yang, G. 2015. Rapid reductive degradation of aqueous p-nitro phenol using nanoscale zero-valent iron particles immobilized on mesoporous silica with enhanced ant oxidation effect. Journal of Applied Surface Science. 333 : 220–228.

Tay, T., Ceylan, B., Erdem, M. and Karagoz, S. 2012. Adsorption of methylene blue from aqueous solution on activated carbon produced from soybean oil cake by KOH activation. Journal of Bio Resources. 7(3): 3175-3187.

Terrado, E., Martinez, M. T., Munoz, E., Redrado, M., Maser, W. K. and Benito, A. M. 2006. Carbon nanotube growth on cobalt-sprayed substrates by thermal CVD. Journal of Materials Science and Engineering: C. 26 (5-7) : 1185–1188.

Todorova, E. V., Djambazov, S.P. andChernev, G.E. 2014. Structure and properties of functionalizedporous silica hybrid materials.Open Journal of Inorganic Non-Metallic Materials. 4: 35-43.

Tumsek, F., Koyuncui, Z., Bodur, G. and Bayindir, Z. 2015. Adsorption of 2,4,6-Trichlorophenol on activated carbon. Journal of The Turkish Chemical Society, section A: Chemistry JOTCSA.2 (3): 22-32.

Udayasoorian, C., Ramalingam, P., Jayabalakrishnan, R. and Vinoth kumar, K. 2013. Carbon supported zero valent iron nanoparticles for treating PCP in Pulp and Paper mill effluent. Research Journal of Chemistry and Environment,17(12): 97-108.

Uddin, M. T., Islam, M.A., Rukanuzzaman, M. and Khan, M.M.R. 2009. Adsorption of methylene blue from aqueous solution by jackfruit (Artocarpus heteropyllus) leaf powder: A fixed bed column study. Journal of Environment Management. 90: 3443- 3450.

Uner, O., Bayrak, Y. and Gecgel, U. 2016. Adsorption of methylene blue by an efficient activated Carbon prepared from Citrullus lanatus Rind: Kinetic, isotherm, thermodynamic and mechanism analysis. Journal of Water Air and Soil pollution. 227:247-262.

Viswanathan, G., Sharon, M. and Bhowmik, S. 2014. Synthesis and characterisation of carbon nano materials from plant derivative. International Journal of Materials, Mechanics and Manufacturing. 2(1) : 25-28.

Wai, C.M., Yak, H. K., Doyle, J.G., Cheng, I.F. and Wenclawiak, B.W. 1999. Reductive de-chlorination of polychlorinated biphenyls by zerovalent iron in subcritical water. Journal of Environmental Science and Technology. 33:1307–10.

Waria, M., Comfort, S.D., Onanong, S., Satapanajaru, T., Boparai, H., Harris, C., 2009. Field-scale clean-up of atrazine and cyanazine contaminated soil with a combined chemical–biological approach. Journal of Environment Qualm. 38:1803–1811.

Wan, Y. and Zhao , D. 2007. On the controllable soft-templating approach to mesoporous silicates. Journal of Chemistry Rev.107, (7): 2821–60.

Wang, S., Zhu, Z. H., Boyjoo, Y. and Choueib, A. 2005. Removal of dyes from aqueous solution using fly ash and red mud. Journal of Water Research. 39(1): 129-138.

Wang, W., Wang, X., Zhou, M., Yue, J. and Mao, Q. 2010. Novel NaY zeolite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst. Journal of Catalysis Communications. 11 : 937–941.

Wang, X., Yang, L., Guo.,Y.,Cheng, X., Zhao, J. and Han, M. 2012. Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. Environmental & Analytical Toxicology. Journal of Environ.AnalyticaToxicolgy.2 (7):2-7.

Wang, L. and Li, J. 2013. Removal of methylene blue from aqueous solution by adsorption onto Crofton Weed Stalk. Journal of Bio Recourse.8 (2): 2521-2536.

Wang, P., Cao, M., Qian, J., Wang, Ch., Ao, Y. and Hou, J. 2014. Kinetics and thermodynamics of adsorption of methylene blue by a magnetic graphene-carbon nanotube composite. Journal of Applied Surface Science.290: 116-124.

Wang, P., Zhang, Y., Meng, Q., Long, H. Wei, R. and Yu, S. 2016. Microscopic study on the interior and exterior reactions of coke with CO_2 and H_2O.Ironmaking & Steelmaking Processes, Products and Applications.19:1-6.

Waria, M., Comfort, S.D., Onanong, S., Satapanajaru, T., Boparai, H., Harris, C., 2009. Field-scale clean-up of atrazine and cyanazine contaminated soil with a combined chemical–biological approach. Journal of Environ Qualm . 38:1803–1811.

Weng, C.H. and Pan, Y.F. 2006. Adsorption characteristics of methylene blue from aqueous solution by sludge ash. Journal of Colloids Surfaces Physicochemical. Engnieering Aspect. 274: 154-162.

Wu, X., Huib, K. N., Lee, S. K., Huia, K. S., Hwang, D. H., Chen, R., Zhoud, W., Son, Y. G. and Cho, Y. R. 2012. Adsorption of basic yellow 87 from aqueous solution onto two different mesoporous adsorbents. Chemical Engineering Journal.180: 91-98.

Wu, G., Li, Ch.,Wang, W., Wu, W., Zan, W. and Wang, X. 2013. Nanosized ZSM-5 zeolites: Seed-induced synthesis and the relation between the physicochemical properties and the catalytic performance in the alkylation of naphthalene. Journal of Microporous and Mesoporous Materials. 180: 187–195.

Wu, L., Liao, L.,Qin, F. and Lv, G. 2015. Stability and pH-independence of nano-zero-valent iron intercalated montmorillonite and its application on Cr(VI) removal. Journal of Contaminant Hydrology. 179:1–9.

Yaacob, W. Z. W., Samsudin, A. R. and Kamaruzaman, N. 2012. Development of nano-zero valent iron for the remediation of contaminated water. Chemical Engineering Transactions. 28: 25–30.

Yaacob, W.Z.W. and How, H. K. 2015. Synthesis and characterization of Marine Clay-supported nano zero valent iron. American Journal of Environmental Sciences. 11 (2): 115-124.

Yokoi, T., Seo, S., Chino, N., Shimojima, A., Okubo, T. 2009. Preparation of silica/ carbon composites with uniform and well-ordered mesopores by esterification method. Journal of Microspore and Mesopore Materals.124 (1–3):123–30.

Yoo, B. Y., Myung, N. V., Hernandez, S. K. , Koo, B. and Rheem, Y. 2007. Electrochemically fabricated zero-valent iron, iron–nickel, and iron–palladium nanowires for environmental remediation applications. Journal of Water Science and Technolology. 55: 149–156.

Zaker, Y., Islam, T.S.A.and Hossain, M. A. 2013. Effect of various factors on the adsorption of methylene blue on siltfractionated from Bijoypur soil, Bangladesh International Research Journal of Environment Sciences. 2 (6):1-7.

Zhang, B. and Yan, N. 2013.Towards rational design of nanoparticle catalysis in ionic liquids. Catalysts Journal. 3: 543-562.

Zhang, Y., Zhou, Ch., and Zhang, L. 2013. Review of chemical vapour deposition of Graphene and related applications. Accounts of chemical research.46 (10): 2329–2339.

Zhang, G., Liu, H., Qu, J., Wu, R. and Cooper,A.T. 2007. $CuFe_2O_4$/activated carbon composite: A novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration. Chemosphere Journal. 68:1058–1066.

Zhua, H., Wang, H., Wu, X. and Jia, Y. 2009. Removal of arsenic from water by supported nano zero-valent iron on activated carbon. Journal of Hazardous Materials. 172: 1591-1596.