UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF ZINC OXIDE/ CLAY MINERALS NANOCOMPOSITES AS ADSORBENT FOR REMOVAL OF Cu(II) AND Pb(II) Ions

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By

HANNATU ABUBAKAR SANI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

This piece of work is dedicated to my entire family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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February 2017

Chairman : Professor Mansor B. Ahmad, PhD
Faculty : Science

Rapid industrialization and population growth has led to the excessive release of toxic metals from agricultural and industrial activities into the environment which poses threat to ecosystem and environment in general. These toxic metals have to be effectively removed before their discharge into water bodies by economically feasible adsorbent. Clay minerals are potentially low cost materials from abundant natural resources which have the ability to accommodate new species in their structure which are of great importance in developing nanocomposites.The aim of this research is to prepare, characterize and test the adsorption efficiency of the prepared nanocomposites. In this study zinc oxide nanoparticle (ZnO-NP) was successfully incorporated into clay minerals montmorillonite (MMT) and talc by a simple green heating method using zinc nitrate and sodium alginate as zinc oxide precursor and stabilizer respectively.The prepared nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Energy Dispersal X-ray (EDAX), Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The potentials of the prepared ZnO/MMT and ZnO/talc nanocomposites as adsorbent for the removal of copper and lead ions from their aqueous solution were investigated. The effect of the pH of the solution, adsorbent dosage, contact time, and different initial concentration on the adsorption efficiency was studied systematically. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data while Langmuir andFreundlichwere used for the isotherm.

XRD and FESEM analyses revealed the presence of ZnO nanoparticles with hexagonal wurtzite structure in the nanocomposites.Energy dispersive X-ray (EDX) also confirmed the presence of ZnO nanoparticles in the nanocomposites. The percentage removal of by ZnO/MMT was found to be 97.2% (Pb) and 89.5% (Cu) which are higher than that of 90.3% (Pb) and 80.6 % (Cu) for ZnO/talc. Kinetics studies revealed that the adsorption of Cu(II) and Pb(II) onto the prepared

nanocomposites followed the pseudo-second order kinetics. The adsorption equilibrium data fitted well to Langmuir isotherm model.Maximum adsorption capacities for the ZnO/MMT and ZnO/talc at pH of 4 were 88.50 and 48.30 mg/g for

Pb(II) and 54.06 and 83.30 mg/g forCu(II), respectively.The regeneration revealed that the nanocomposites adsorbent can be utilized for more than three times. They can serve as promising adsorbents for the removal of Cu(II) and Pb(II)lead ions from aqueous solutions because of their distinctive chemical and physical properties.Electrostatic attraction and ion exchangecould be the main adsorption mechanisms for lead and copper ions adsorption onto the nanocomposites. Thermodynamics results revealed that the adsorption was an exothermic process. The experimental results showed that the nanocomposites have high level of adsorption towards heavy metal ions. Consequently, it is concluded that the prepared nanocomposites (ZnO/MMT and ZnO/talc) can be used for the removal of the heavy metal ions from the aqueous solutions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN NANOZARAH ZINK OKSIDA DALAM MINERAL TANAH LIAT UNTUK PENYINGKIRAN LOGAM BERAT

Oleh

HANNATU ABUBAKAR SANI

Februari 2017

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Perindustrian dan pertumbuhan penduduk yang pesat telah membawa kepada pembebasan berlebihan logam toksik daripada aktiviti pertanian dan perindustrian ke dalam alam sekitar yang menimbulkan ancaman kepada ekosistem dan alam sekitar secara umum. Logam toksik ini perlu dikeluarkan dengan berkesan sebelum dilepaskan ke dalam saliran air oleh bahan penjerap secara efektif dan ekonomik. Mineral tanah liat bahan kos rendah yang berpotensi dari sumber asli yang banyak mempunyai keupayaan untuk menampung spesies baru dalam struktur mereka yang memberi kepentingan yang besar dalam membangunkan nanokomposit. Tujuan kajian ini adalah untuk menyediakan, mencirikan dan menguji kecekapan penjerapan daripada nanocomposites bersedia. Dalam kajian ini zink oksida nanoparticle (ZnO-NP) telah berjaya dimasukkan ke dalam mineral tanah liat montmorilonit (MMT) dan talkum oleh kaedah pemanasan hijau mudah menggunakan nitrat zink dan natrium alginate masing-masing sebagai pelopor zink oksida dan penstabil. The nanokomposit bersedia telah disifatkan oleh spektroskopi inframerah jelmaan Fourier (FTIR), pembelauan sinar-X (XRD), Tenaga Penyuraian sinar-X (EDAX), mikroskopi imbasan pancaran elektron (FESEM) dan mikroskopi elektron penghantaran (TEM). Potensi yang disediakan ZnO/MMT dan ZnO/nanokomposit talkum sebagai penjerap untuk penyingkiran kuprum dan ion plumbum daripada larutan akueus mereka telah disiasat. Kesan pH daripada penyelesaian, penjerap dos, masa sentuhan, dan kepekatan awal yang berbeza kepada kecekapan penjerapan telah dikaji secara sistematik. Model kinetik pseudo-tertib-pertama dan pseudo-tertib-kedua telah digunakan untuk menggambarkan data kinetik manakala Langmuir dan Freundlich telah digunakan untuk untuk isoterma.

Analisis XRD dan FESEM mendedahkan kehadiran nanozarah ZnO dengan struktur wurtzit heksagon dalam nanokomposit. Serakan tenaga Sinar-X (EDX) juga mengesahkan kehadiran nanozarah ZnO dalam nanokomposit. Penyingkiran peratusan oleh ZnO/MMT iaitu 97.2% (Pb) dan 89.5% (Cu) adalah lebih tinggi daripada 90.3% (Pb) dan untuk ZnO/Talkum 80.6% (Cu). Kajian kinetik

mendedahkan bahawa penjerapan Cu(II) dan Pb(II) dalam nanokomposit yang disediakan mengikuti kinetik pseudo-tertib-kedua dan data keseimbangan penjerapan adalah mengikuti model isoterma Langmuir. Kapasiti penjerapan maksimum bagi ZnO/MMT dan ZnO/Talkum pada pH 4 adalah masing-masing 88.50 dan 48.30 mg/g untuk Pb^{2+} dan 54.06 dan 83.30 mg/g untuk Cu^{2+}. Penjanaan semula itu mendedahkan bahawa penjerap nanokomposit yang boleh digunakan untuk tiga kali. Mereka boleh digunakan sebagai adsorben menjanjikan untuk penyingkiran ion kuprum dan plumbum daripada larutan akueus kerana ciri kimia dan fizikal yang luar biasa. Tarikan elektrostatik dan penukaran ion boleh menjadi mekanisme penjerapan utama untuk ion plumbum dan ion kuprum penjerapan ke atas nanokomposit. Keputusan termodinamik mendedahkan bahawa penjerapan adalah satu proses eksotermik. Keputusan eksperimen menunjukkan nanokomposit mempunyai tahap tinggi penjerapan ke arah ion logam berat. Oleh itu, dapat disimpulkan bahawa nanokomposit disediakan (ZnO/MMT dan ZnO/Talkum) boleh digunakan untuk penyingkiran ion logam berat dalam larutan akueus.

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I certify that a Thesis Examination Committee has met on 22 February 2017 to conduct the final examination of Hannatu Abubakar Sani on her thesis entitled "Preparation and Characterization of Zinc Oxide/Clay Minerals Nanocomposites as Adsorbent for Removal of Cu(II) and Pb(II) Ions" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
EDX	Energy dispersive x-ray
FESEM	Field emission scanning electron microscopy
FT-IR	Fourier transform infrared
MMT	Montmorillonite
NC	Nanocomposites
PXRD	Powder x-ray diffraction
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV-vis	Ultraviolet-visible
ZnO/MMT	Zinc oxide/ Montmorillonite
ZnO/Talc	Zinc oxide/Talc
ZnONPs	Zinc oxide nanoparticles

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Nanotechnology is a branch of science that deals with fabrication, characterization, production, application and exploration of materials and devices in nano size ranging from 1 to 100nm (Mansoori*et al*., 2008). An internationally accepted meaning for nanoparticles does not exist. Nanotechnology have different meanings, with National Nanotechnology Initiative of the USA, defining nanotechnology as research and technology development at the atomic, molecular, or macromolecular levels using a length scale of approximately one to one hundred nanometer in any dimension; the creation and use of structures, devices and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on an atomic scale (USEPA, 2007)). Research in nanotechnology is now a hot spot in modern science as new different kind of applications in the area of science and technology are derived from it(Sirelkhatim*et al*., 2015). Nanotechnology has the potential to have huge impacts on many industries and a times described as a general purpose technology because it has important effects on almost all industries and all areas of society such as mechanics, electronics, optics, medicine, plastics, energy, aerospace and environmental remediation (Bhattacharyya *et al.,* 2009; Bhattacharyya and Ali, 2008 ;Xu *et al*., 2012).Nanocomposites are composite multiphase materials in which one of the phases has at least one dimension that is in the nano scale level and the structure of nanocomposites can be defined one dimensional, two dimensional and three dimensional(Oliveira and Machado, 2013; Zeng *et al*., 2002;Jeon and Baek, 2010). The combined constituent's materials that made up the nanocomposites have different physical or chemical properties and produced materials with different properties from the individual constituents. Applications of nanocomposites cover the following key areas environmental remediation, transportation and safety, catalysis, information industry and many more. Clay minerals are potentially low cost materials from abundant natural resources which have the ability to accommodate new species in their structure which are of great importance in developing nanocomposites that are widely used in industrial and environmental applications. Clay mineral modification by chemical and physical method increases their potentials for many applications such as adsorbent, catalyst etc. Montmorillonite (MMT) and talc are members of clay minerals. The semiconductor zinc oxide (ZnO) is a favorable material because of its various properties and various applications, ranging from adsorption and photo catalytic(Nohavica and Gladkov, 2010), anti-bacterial (Ramesh*et al*., 2015), catalyst, adsorbent, optical, semiconducting and gas sensor.Application of nanotechnology in the aspect of environment has fix problems arising from environmental issues; provide measures that would prevent future problem arising from the interactions of energy and materials with the environment and any potential hazard that might be posture nanotechnology itself (Mansoori*et al*.,2008).

Environmental pollution is one of the problems worldwide that is of great concern as the natural ecosystem is deteriorated. Generated waste water from industries and

agricultural activities contains different toxic heavy metals which are non-degradable and thereby tend to accumulate in humans and causes detrimental effects to health. These heavy metals are toxic to humans and the ecosystem when their tolerance limit is exceeded (Bulgariu*et al*., 2015). These metals need to be properlyremoved before discharging them into the environment. The primary sources of toxic heavy metals into the environment occur though industrial activities, agricultural activities and indiscriminate dumping of waste (Meena *et al*., 2005). Nanotechnology have an important role to play by creating new opportunities to shape the environment in terms of developing efficient, low cost friendly adsorbent with high surface area, volume ratio, low toxicity, selectivity and biodegradable making them good adsorbent for heavy metals ions removal from waste water. The techniques for treatment, purification and remediation and sensors for monitoring purpose are also developed from the technology whichimproves the quantity and the quality of water resources (Singh*et al*., 2013).

1.2 Problem statement

Rapid industrialization and population growth has led to the excessive release of toxic metals from agricultural and industrial activities into the environment which poses threat to ecosystem and environment in general. A number of techniques have been used for toxic metal removal from wastewater which includes chemical precipitation ion exchange electrolytic etc. These methods have been found to be limited, because of the high capital and operating costs and ineffectiveness in meeting stringent effluent standards. Improving the efficiency of clay materials to produce nanocomposites with high efficiency and high surface area will be applied as an adsorbent for the removal of toxic metals. The novelty of this research is the improvements of clay mineral by ZnO stabilize by sodium alginate for toxic metal removal.

In this research zinc oxide nanoparticles were prepared by heat method using zinc nitrate and sodium alginate as zinc oxide precursor and stabilizer respectively. The prepared nanoparticles were characterized so as to ascertain the formation of the nanoparticles. Nanocomposites were later prepared by adding the mixture of zinc precursor and stabilizer to montmorillonite and talc to form zinc oxide/montmorillonite and Zinc oxide/talc nanocomposites. The surface morphology, crystallinity, functional group and surface area were used to investigate by powder x-ray diffraction (PXRD),Fourier transform infrared(FTIR),Field Emission Scanning Electron microscopy(FESEM),Transmission Electron Microscopy(TEM) and BET. The potential of the prepared nanocomposites were studied for the adsorption of heavy metal ions (copper and lead) from an aqueous solution. The effect adsorbent dosage, contact time, initial concentration and solution pH on the adsorption efficiency were studied thoroughly.

1.3 Project objectives

The aim of this study is to prepared nanocomposites from ZnO and clay materials by heat method for heavy metals removal. The scope of my research includes and limited to synthesizing ZnO nanoparticle and ZnO/montmorillonite and ZnO/talc

nanocomposites by simple heat method using sodium alginate as a stabilizer .The prepared nanoparticle and nanocomposites would be characterize using various procedures to determine their properties. The characterized nanocomposites would be applied for heavy metal ions uptake from aqueous solution by batch adsorption method.

Specific research objectives include:

1. To prepare ZnO nanoparticles,ZnO/MMT and ZnO/Talc nanocomposites by heat method
2. To characterize the prepared nanoparticles and nanocomposites
3. To determine the adsorption capacity of the prepared nanocomposites ZnO/MMT-NCs and ZnO/talc-NCs using batch method to remove heavy metals (lead and copper ion).
4. To compared the adsorption capacities of ZnO/MMT-NCs and ZnO/talc nanocomposites

REFERENCES

AbdElhady, M. M. (2012). Preparation and characterization of chitosan/zinc oxide nanoparticles for imparting antimicrobial and UV protection to cotton fabric. *International Journal of Carbohydrate Chemistry,* 2012, 1-6

Abdel Wahab, O. (2007). Kinetic and isotherm studies of copper (II) removal from wastewater using various adsorbents, *Egyptian Journal of Aquatic Research,* 33(1), 125–42.

Acharya, J., Sahu, J. N., Mohanty, C. R., and Meikap, B. C. (2009). Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. *Chemical Engineering Journal*, *149*(1), 249-262.

Ahmad, R., Kumar, R., and Haseeb, S. (2012). Adsorption of Cu^{2+} from aqueous solution onto iron oxide coated eggshell powder : Evaluation of equilibrium , isotherms , kinetics , and regeneration capacity, *Arabian Journal of Chemistry,* 5(3), 353–59.

Aitken, R., Chaudhry, M. Q., Boxall, A. B. A., and Hull, M. (2006). Manufacture and use of nanomaterials: current status in the UK and global trends. *Occupational Medicine*, *56*(5), 300-306.

Alansi, A. M., Alkayali, W. Z., Al-qunaibit, M. H., Qahtan, T. F., and Saleh, T. A. (2015). Synthesis of exfoliated polystyrene/anionic clay MgAl-layered double hydroxide: structural and thermal properties. *RSC Advances*, *5*(87), 71441-71448.

Aljendeel, H. A. (2011). Removal of heavy metals using reverse osmosis, *Journal of Engineering* 17(3), 647–58.

Alshabanat, M. (2013). Characterization and mechanical properties study of intercalated Talc/Polypropylene nanocomposites, *Journal of American Science,* 9(3), 322–26.

Al-Shalalfeh, M. M., Saleh, T. A., and Al-Saadi, A. A. (2016). Silver colloid and film substrates in surface-enhanced Raman scattering for 2-thiouracil detection. *RSC Advances*, *6*(79), 75282-75292.

Alswat, A. A., Ahmad, M. B., and Saleh, T. A. (2016). Zeolite modified with copper oxide and iron oxide for lead and arsenic adsorption from aqueous solutions. *Journal of Water Supply: Research and Technology-Aqua*, *65*(6), 465-479.

Alyüz, B., and 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*(1), 482-488.

Amarasinghe, B. M. W. P. K., and Williams, R. A. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, *132*(1), 299-309.

Anirudhan, T. S., and Radhakrishnan, P. G. (2008). Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell. *The Journal of Chemical Thermodynamics*, *40*(4), 702-709.

Arbabi, M., Hemati, S., and Amiri, M. (2015). Removal of lead ions from industrial wastewater : A review of removal methods. *International Journal of Epidemiologic Research,* 2(2), 105–9.

Argun, M. E., Dursun, S., Ozdemir, C., and Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of hazardous materials*, *141*(1), 77-85.

Arora, A. K., Devi, S., Jaswal, V. S., Singh, J., Kinger, M., and Gupta, V. D. (2014). Synthesis and characterization of ZnO nanoparticles. *Oriental Journal of Chemistry*, *30*(4), 1671-1679.

Avella, M., De Vlieger, J. J., Errico, M. E., Fischer, S., Vacca, P., and Volpe, M. G. (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*, *93*(3), 467-474.

Aydın, H., Bulut, Y., and Yerlikaya, Ç. (2008). Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management*, *87*(1), 37-45.

Azizi, S., Ahmad, M. B., Namvar, F., and Mohamad, R. (2014). Green biosynthesis and characterization of zinc oxide nanoparticles using brown marine macroalga sargassum muticum aqueous extract. *Materials Letters,* 116, 275–77.

Babel, S., and Kurniawan, T. A. (2003). Low-Cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials,* 97(1-3), 219–43.

Bagheri, S., Chandrappa, K. G., and Hamid, S. B. A. (2013). Facile synthesis of nano-sized ZnO by direct precipitation method. *Der Pharma Chemica*, *5*(3), 265-270

Bai, Y., and Bartkiewicz, B. (2009). Removal of Cadmium from wastewater using ion exchange resin amberjet 1200H columns. *Polish Journal of Environmental Studies.* 18(6): 1191–95.

Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999). Review paper a Review of potentially low-cost sorbents for heavymetals. *Water Resources,* 33(11).

Banerjee, P., Chakrabarti, S., Maitra, S., and Dutta, B. K. (2012). Zinc oxide nano-particles–sonochemical synthesis, characterization and application for photo-remediation of heavy metal. *Ultrasonics Sonochemistry*, *19*(1), 85-93

Banerjee, S. S., and Chen, D. H. (2007). Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. *Journal of Hazardous Materials*, *147*(3), 792-799.

Barakat, M. A. (2011). New Trends in Removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry,* 4(4), 361–77.

Barick, K. C., Singh, S., Aslam, M., and Bahadur, D. (2010). Porosity and photocatalytic studies of transition metal doped ZnO nanoclusters. *Microporous and Mesoporous Materials*, *134*(1), 195-202.

Baruwati, B., Kumar, D. K., and Manorama, S. V. (2006). Hydrothermal synthesis of highly crystalline ZnO nanoparticles: A competitive sensor for LPG and EtOH. *Sensors and Actuators B: Chemical*, *119*(2), 676-682.

Baysal, A., Ozbek, N., and Akman, S. (2013). Determination of trace metals in waste water and their removal processes. INTECH Open Access Publisher 145-171.

Becheri, A., Dürr, M., Nostro, P. L., and Baglioni, P. (2008). Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers. *Journal of Nanoparticle Research*, *10*(4), 679-689

Bhardwaj, D., Sharma, P., and Khare, P. S. (2013). Synthesis of whorl shaped zinc oxide nanostructure crystals by simple wet synthesis route. *Materials Letters*, *111*, 134-136.

Bhattacharyya, D., Singh, S., Satnalika, N., Khandelwal, A., and Jeon, S. H. (2009). Nanotechnology, big things from a tiny world: a review. *Nanotechnology*, *2*(3), 29-38

Bhattacharyya, K. G., and Gupta, S. S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in Colloid And Interface Science*, *140*(2), 114-131.

Bu, I. Y., and Cole, M. T. (2013). One-pot synthesis of intercalating ZnO nanoparticles for enhanced dye-sensitized solar cells. *Materials Letters*, *90*, 56-59.

Bulgariu, L., Bulgariu, D., and Rusu, C. (2015). Marine algae biomass for removal of heavy metal ions. In *Springer Handbook of Marine Biotechnology* , 611-648).

Carp, O., Jurca, B., Ene, R., Somacescu, S., and Ianculescu, A. (2015). Biopolymer starch mediated synthetic route of multi-spheres and donut ZnO structures. *Carbohydrate Polymers*, *115*, 285-293.

Chang, Y. P., Ren, C. L., Qu, J. C., and Chen, X. G (2012). Applied surface science preparation AND characterization of Fe_3O_4 / graphene nanocomposite and investigation of its adsorption performance for aniline and P -chloroaniline. *Applied Surface Science,* 261, 504–9.

Charnay, C., Lagerge, S., and Partyka, S. (2001). Assessment of the surface heterogeneity of talc materials. *Journal of colloid and interface science*, *233*(2), 250-258.

Chen, J., Feng, J., and Yan, W. (2016). Influence of metal oxides on the adsorption characteristics of PPy/metal oxides for Methylene Blue. *Journal of Colloid and Interface Science*, *475*, 26-35.

Cho, J. M., Song, J. K., and Park, S. M. (2009). Characterization of ZnO nanoparticles grown by laser ablation of a Zn target in neat water, *Bulletin of the Korean Chemical Society* 30(7), 1616–18.

Choina, J., Bagabas, A., Fischer, C., Flechsig, G. U., Kosslick, H., Alshammari, A., and Schulz, A. (2015). The influence of the textural properties of ZnO nanoparticles on adsorption and photocatalytic remediation of water from pharmaceuticals. *Catalysis Today*, *241*, 47-54.

Dabrowski, A., Hubicki, Z., Podkościelny, P., and Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere,* 56(2), 91–106.

Damonte, L. C., Zélis, L. M., Soucase, B. M., and Fenollosa, M. H.(2004). "Nanoparticles of ZnO obtained by mechanical milling. *Powder Technology* 148, 15–19.

Danmaliki, G. I., and Saleh, T. A. (2017). Effects of bimetallic Ce/Fe nanoparticles on the desulfurization of thiophenes using activated carbon. *Chemical Engineering Journal*, *307*, 914-927

Darroudi, M., Sabouri, Z., Oskuee, R. K., Zak, A. K., Kargar, H., and Hamid, M. H. N. A. (2013). Sol–gel synthesis, characterization, and neurotoxicity effect of zinc oxide nanoparticles using gum tragacanth. *Ceramics International*, *39*(8), 9195-9199.

Dawodu, F. A., and Akpomie, K. G. (2014). Simultaneous adsorption of Ni (II) and Mn (II) ions from aqueous solution unto a Nigerian kaolinite clay. *Journal of Materials Research and Technology*, *3*(2), 129-141.

Demiral, H., and Güngör, C. (2016). Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse. *Journal of Cleaner Production*, *124*, 103-113

Desta, M. B. (2013). Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (Eragrostis tef) agricultural waste. *Journal of Thermodynamics*,1(1) 1-7.

Đukić, A. B., Kumrić, K. R., Vukelić, N. S., Dimitrijević, M. S., Baščarević, Z. D., Kurko, S. V., and Matović, L. L. (2015). Simultaneous removal of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} from highly acidic solutions using mechanochemically synthesized Montmorillonite–Kaolinite/TiO_2 composite. *Applied Clay Science*, *103*, 20-27.

Dumas, A., Mizrahi, M., Martin, F., and Requejo, F. G. (2015). Local and extended-order evolution of synthetic talc during hydrothermal synthesis: Extended X-ray absorption fine structure, X-ray diffraction, and fourier transform infrared spectroscopy studies. *Crystal Growth and Design*, *15*(11), 5451-5463.

Ely, A., Baudu, M., Kankou, M. O. S. A. O., and Basly, J. P. (2011). Copper and nitrophenol removal by low cost alginate/Mauritanian clay composite beads. *Chemical Engineering Journal*, *178*, 168-174.

Espitia, P. J. P., Soares, N. D. F. F., dos Reis Coimbra, J. S., de Andrade, N. J., Cruz, R. S., and Medeiros, E. A. A. (2012). Zinc oxide nanoparticles: synthesis, antimicrobial activity and food packaging applications. *Food and Bioprocess Technology*, *5*(5), 1447-1464.

Fadhil, F. A., and Hadi ,I. H. (2015). Preparation and characterization of zinc oxide nanoparticles by laser ablation of zinc in isopropanol. *Engineering and Technology Journal,* 3(5), 791–98.

Fan, Z., and Lu, J. G. (2005). Zinc oxide nanostructures: synthesis and properties. *Journal of Nanoscience and Nanotechnology*, *5*(10), 1561-1573.

Farghali, A. A., Bahgat, M., Allah, A. E., and Khedr, M. H. (2013). Adsorption of Pb (II) ions from aqueous solutions using copper oxide nanostructures. *Beni-Suef University Journal of Basic and Applied Sciences*, *2*(2), 61-71.

Fatimah, I., Huda, T., Palaniappan, L., Hussain, A., Begum, A., and Rahman, A. (2012). AV Adedayo. *Asian Journal of Materials Science*, *4*(1), 13-20.

Fatimah, I., Wang, S., and Wulandari, D. (2011). ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue. *Applied Clay Science*, *53*(4), 553-560.

Farmer, V.C., and J.D. Russel. 1967. “Infrared absorption spectroscopy in clay studies: vibrations of the hydroxyl group.” *Clays and Clay Minerals* 15: 121–41.

Feng, Y. S., Zhou, S. M., Li, Y., Li, C. C., and Zhang, L. D. (2003). Synthesis and characterization of tin oxide nanoparticles dispersed in monolithic mesoporous silica. *Solid State Sciences*, *5*(5), 729-733.

Fu, F., and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management,* 92(3), 407–18.

Ge, F., Li, M. M., Ye, H., and Zhao, B. X. (2012). Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles. *Journal of Hazardous Materials*, *211*, 366-372.

Gil, A., Korili, S. A., Trujillano, R., and Vicente, M. A. (Eds.). (2010). Pillared clays and related catalysts. New York, NY: Springe

Gnanasangeetha, D., and SaralaThambavani, D. (2013). One pot synthesis of zinc oxide nanoparticles via chemical and green method. *Research Journal of Material Sciences,* 1(7), 1–8.

Guillén, G. G., Palma, M. M., Krishnan, B., Avellaneda, D., Castillo, G. A., Roy, T. D., and Shaji, S. (2015). Structure and morphologies of ZnO nanoparticles synthesized by pulsed laser ablation in liquid: Effects of temperature and energy fluence. *Materials Chemistry and Physics*, *162*, 561-570

Gunalan, S., Sivaraj, R., and Rajendran, V.(2013). Green Synthesized ZnO Nanoparticles against Bacterial and Fungal Pathogens. *Progress in Natural Science: Materials International,* 22(6), 693–700.

Gunatilake, S K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies,* 1(1), 12–18.

Günay, A., Arslankaya, E., and Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *146*(1), 362-371

Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A., and Agarwal, S . (2012). chemical treatment technologies for waste-water recycling—an Overview. *Rsc Advances,* 2(16), 6380–88.

Gupta, V. K., Agarwal, S., and Saleh, T. A. (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., and Ali, I. (2004). Removal of lead and chromium from wastewater using bagasse Fly Ash - A Sugar Industry Waste. *Journal of Colloid and Interface Science,* 271(2), 321–28.

Gupta, V. K., Gupta, M., and Sharma, S. (2001). Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste. *Water research*, *35*(5), 1125-1134.

Harishanand, K. S., Nagabhushana, H., Nagabhushana, B. M., Panda, P., Gupta, R., Muruli, M. S ,and Mahesh, K. V. (2013). Comparitive study on mechanical properties of ZnO , ZrO_2 and CeO_2 nanometal oxides reinforced epoxy composites. *Advances in Polymer Science and Technology,* 3(1), 7–13.

Hasan, S. (2015). A Review on Nanoparticles : Their synthesis and types. *Research Journal of Recent Sciences,* 4, 9–11.

He, Lili, Yang Liu, Azlin Mustapha, and Mengshi Lin. (2011). Antifungal activity of zinc oxide nanoparticles against botrytis cinerea and penicillium expansum, *Microbiological Research,* 166(3), 207–15.

Ho, Y. S. (2006). Isotherms for the sorption of lead onto Peat: comparison of linear and non-linear methods. *Polish Journal of Environmental Studies,* 15(1), 81–86.

Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., and Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *Journal of Hazardous Materials*, *211*, 317-331.

Huang, H., Yuan, Q., and Yang, X. (2004). Preparation and characterization of metal-chitosan nanocomposites. *Colloids and Surfaces B: Biointerfaces,* 39(1-2), 31–37.

Hur, S. G., Kim, T. W., Hwang, S. J., Hwang, S. H., Yang, J. H., and Choy, J. H. (2006). Heterostructured nanohybrid of zinc oxide-montmorillonite clay. *The Journal of Physical Chemistry. B* 110(4), 1599–1604.

Hussain, F., Hojjati, M., Okamoto, M., and Gorga, R. E. (2006). Polymer-Matrix Nanocomposites, Processing, Manufacturing, and Application. *Polymer Science,* 40(17), 27–32.

Jagung, P. T. (2011). Removal of Zn (II), Cd (II) and Mn (II) from aqueous solutions by adsorption on maize stalks. *Malaysian Journal of Analytical Sciences*, *15*(1), 8-21.

Jalal, R., Goharshadi, E. K., Abareshi, M., Moosavi, M., Yousefi, A., and Nancarrow, P. (2010). ZnO nanofluids: green synthesis, characterization, and antibacterial activity. *Materials Chemistry and Physics*, *121*(1), 198-201.

Jayaseelan, C., Rahuman, A. A., Kirthi, A. V., Marimuthu, S., Santhoshkumar, T., Bagavan, A., and Rao, K. B. (2012). Novel microbial route to synthesize ZnO nanoparticles using Aeromonas hydrophila and their activity against pathogenic bacteria and fungi. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *90*, 78-84..

Jeon, I. Y., and Baek, J. B. (2010). Nanocomposites Derived from Polymers and Inorganic Nanoparticles. *Materials* 3: 3654–74.

Joshi, M., Bhattacharyya, A., and Ali, S. W. (2008). Characterization techniques for nanotechnology application in textiles. *Indian Journal of Fibre and Textile Research,* 33(3), 304–17.

Kakuta, S., and Abe, T. (2009). Photocatalytic activity of Cu_2O nanoparticles prepared through novel synthesis method of precursor reduction in the presence of thiosulfate. *Solid State Sciences*, *11*(8), 1465-1469.

Kalantari, K. (2013). Synthesis of talc/Fe. *International Journal of Nanomedicine*, *8*, 1817-1823.

Karnitz, O., Gurgel, L. V. A., De Melo, J. C. P., Botaro, V. R., Melo, T. M. S., de Freitas Gil, R. P., and Gil, L. F. (2007). Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresource technology*, *98*(6), 1291-1297

Kang, S. Y., Lee, J. U., Moon, S. H., and Kim, K. W. (2004). Competitive adsorption characteristics of Co $^{2+}$, Ni $^{2+}$, and Cr $^{3+}$ by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere*, *56*(2), 141-147.

Karaca, M., Kıranşan, M., Karaca, S., Khataee, A., and Karimi, A. (2016). Ultrasonics sonochemistry sonocatalytic removal of naproxen by synthesized zinc oxide nanoparticles on montmorillonite. *Ultrasonics Sonochemistry,* 31, 250–56.

Khaorapapong, N., Khumchoo, N., and Ogawa, M. (2011). Preparation of zinc oxide – montmorillonite hybrids. *Materials Letters,* 65(4), 657–60.

Khaorapapong, N., Khumchoo, N., and Ogawa, M. (2015). Preparation of copper oxide in smectites. *Applied Clay Science* 104, 238–44.

Kharissova, O. V., Dias, H. R., Kharisov, B. I., Pérez, B. O., and Pérez, V. M. J. (2013). The greener synthesis of nanoparticles. *Trends in Biotechnology*, 31(4), 240-248.

Khataee, A., Kiranşan, M., Karaca, S., & Arefi-Oskoui, S. (2016). Preparation and characterization of ZnO/MMT nanocomposite for photocatalytic ozonation of a disperse dye. *Turkish Journal of Chemistry*, *40*(4), 546-564

Khoshhesab, Z. M., Sarfaraz, M., and Asadabad, M. A. (2011). Preparation of ZnO nanostructures by chemical precipitation method. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, *41*(7), 814-819.

Khumchoo, N., Khaorapapong, N., and Ogawa, M. (2015). Formation of zinc oxide particles in cetyltrimethylammonium-smectites. *Applied Clay Science,* 105-106, 236–42.

Kołodziejczak-Radzimska, A., and Jesionowski, T. (2014). Zinc oxide—from synthesis to application: a review. *Materials*, *7*(4), 2833-2881

Kocabaş-Ataklı, Z. Ö., and Yürüm, Y. (2013). Synthesis and characterization of anatase nanoadsorbent and application in removal of lead, copper and arsenic from water. *Chemical Engineering Journal*, *225*, 625-635.

Kubilay, Ş., Gürkan, R., Savran, A., and Şahan, T. (2007). Removal of Cu (II), Zn (II) and Co (II) ions from aqueous solutions by adsorption onto natural bentonite. *Adsorption*, *13*(1), 41-51.

Kumar, J. P., Ramacharyulu, P. V. R. K., Prasad, G. K., and Singh, B. (2015). Montmorillonites supported with metal oxide nanoparticles for decontamination of sulfur mustard. *Applied Clay Science*, *116*, 263-272.

Kumar, P. S., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., and Sivanesan, S. (2010). Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*, *261*(1), 52-60.

Kumar, P. S., and Kirthika, K. (2009). Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. *Journal of Engineering Science and Technology*, *4*(4), 351-363.

Kumar, S. S., Venkateswarlu, P., Rao, V. R., and Rao, G. N. (2013). Synthesis, characterization and optical properties of zinc oxide nanoparticles. *International Nano Letters*, *3*(1), 1-6.

Kutláková, K. M., Tokarský, J., and Peikertová, P. (2015). Functional and eco-friendly nanocomposite kaolinite/ZnO with high photocatalytic activity. *Applied Catalysis B: Environmental*, *162*, 392-400.

Latif, M. H. A. Preparation and Characterization for a New ZnO-Montmorillonite Hybrid from Iraqi (Traifawi) Clay Minerals. 7(5), 18–24

Lensveld, D. J., Mesu, J. G., Van Dillen, A. J., and de Jong, K. P. (2001). Synthesis and characterisation of MCM-41 supported nickel oxide catalysts. *Microporous and Mesoporous Materials*, *44*, 401-407.

Li, L. H., Deng, J. C., Deng, H. R., Liu, Z. L., and Xin, L. (2010). Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes. *Carbohydrate research*, *345*(8), 994-998

Li, Q., Zhai, J., Zhang, W., Wang, M., and Zhou, J. (2008). A study on adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by peanut husk. *Bulletin of the chemical society of Ethiopia*, *22*(1).

Li, S., Yang, S. C., Zhao, S. L., Li, P., and Zhang, J. (2015). Microwave and acid-modified talc for the adsorption of methylene blue in aqueous solution. *Journal of the Serbian Chemical Society*, *80*(4), 563-574

Lin, F., Zhu, G., Shen, Y., Zhang, Z., and Dong, B. (2015). Study on the modified montmorillonite for adsorbing formaldehyde. *Applied Surface Science*, *356*, 150-156.

Liu, L. E., Liu, J., Li, H., Zhang, H., Liu, J., and Zhang, H. (2012). Equilibrium, kinetic, and thermodynamic studies of lead (II) biosorption on sesame leaf. *BioResources*, *7*(3), 3555-3572.

Liu, yusheng, shimou chen, lei zhong, and guozhong wu. (2009). preparation of high-stable silver nanoparticle dispersion by using sodium alginate as a stabilizer under gamma radiation. *Radiation Physics and Chemistry,* 78(4), 251–55.

Ludi, B., and Niederberger, M. (2013). Zinc oxide nanoparticles: chemical mechanisms and classical and non-classical crystallization. *Dalton Transactions*, *42*(35), 12554-12568.

Ma, L., Zhu, J., Xi, Y., Zhu, R., He, H., Liang, X., and Ayoko, G. A. (2015). Simultaneous adsorption of Cd (II) and phosphate on Al 13 pillared montmorillonite. *RSC Advances*, *5*(94), 77227-77234.

Mahdavi, M., Ahmad, M. B., Haron, M. J., Gharayebi, Y., Shameli, K., and Nadi, B. (2013). Fabrication and characterization of SiO2/(3-aminopropyl) triethoxysilane-coated magnetite nanoparticles for lead (II) removal from aqueous solution. *Journal of Inorganic and Organometallic Polymers and Materials*, *23*(3), 599-607.

Mahdavi, M., Namvar, F., Ahmad, M. B., and Mohamad, R. (2013). Green biosynthesis and characterization of magnetic iron oxide (Fe3O4) nanoparticles using seaweed (Sargassum muticum) aqueous extract. *Molecules*, *18*(5), 5954-5964

Mallakpour, S., and Khadem, E. (2016). Carbon nanotube–metal oxide nanocomposites: Fabrication, properties and applications. *Chemical Engineering Journal*, *302*, 344-367.

Mansoori, G A, T Rohani Bastami, and A Ahmadpour. (2008). Chapter 2 Environmental application of nanotechnology. *American Chemical Science Journal* 2, 1–73.

Martins, M. G., Martins, D. O., de Carvalho, B. L., Mercante, L. A., Soriano, S., Andruh, M., and Vaz, M. G. (2015). Synthesis and characterization of montmorillonite clay intercalated with molecular magnetic compounds. *Journal of Solid State Chemistry*, *228*, 99-104.

Masui, Y., Wang, J., Teramura, K., Kogure, T., Tanaka, T., and Onaka, M. (2014). Unique structural characteristics of tin hydroxide nanoparticles-embedded montmorillonite (Sn-Mont) demonstrating efficient acid catalysis for various organic reactions. *Microporous and Mesoporous Materials*, *198*, 129-138

Mazilu, M., Musat, V., Innocenzi, P., Kidchob, T., and Marongiu, D. (2012). Liquid-phase preparation and characterization of zinc oxide nanoparticles. *Particulate Science and Technology*, *30*(1), 32-42.

Meena, A. K., Mishra, G. K., Rai, P. K., Rajagopal, C., and Nagar, P. N. (2005). Removal of Heavy Metal Ions from Aqueous Solutions Using Carbon Aerogel as an Adsorbent. *Journal of Hazardous Materials* 122(1-2), 161–70.

Meulenkamp, E. A. (1998). Synthesis and growth of ZnO nanoparticles. *The Journal of Physical Chemistry B*, *102*(29), 5566-5572.

Miller, M. (2015). Removal Technologies in Wastewater Treatment.*IWA Publishing.*

Minegishi, K., Koiwai, Y., Kikuchi, Y., Yano, K., Kasuga, M., and Shimizu, A. (1997). Growth of p-type zinc oxide films by chemical vapor deposition. *Japanese Journal of Applied Physics*, *36*(11A), L1453.

Moradhaseli, S., Mirakabadi, A. Z., Sarzaeem, A., Dounighi, N. M., Soheily, S., and Borumand, M. R. (2013). Preparation and characterization of sodium alginate nanoparticles containing ICD-85 (venom derived peptides).*International Journal of Innovation and Applied Preparation*, 4 (3), 534-54.

Murillo-Álvarez, J. I., and Hernández-Carmona, G. (2007). Monomer composition and sequence of sodium alginate extracted at pilot plant scale from three commercially important seaweeds from Mexico. *Journal of Applied Phycology*, *19*(5), 545-548.

Nassar, Nashaat N. (2010). Rapid Removal and Recovery of Pb (II) from Wastewater by Magnetic Nanoadsorbents. *Journal of Hazardous Materials*, 184(1-3), 538–46.

Németh, J., Rodríguez-Gattorno, G., Díaz, D., Vázquez-Olmos, A. R., and Dékány, I. (2004). Synthesis of ZnO nanoparticles on a clay mineral surface in dimethyl sulfoxide medium. *Langmuir*, *20*(7), 2855-2860.

Ngah, W. W., and Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as a review. *Bioresource Technology* *99*(10), 3935-3948.

Nguyen, Q. T., and Baird, D. G. (2006). Preparation of polymer–clay nanocomposites and their properties. *Advances in Polymer Technology*, *25*(4), 270-285.

Nohavica, D., and Gladkov, P. (2010). ZnO nanoparticles and their applications-new achievements. *Olomouc, Czech Republic, EU*, *10*, 12-14.

Nouroozi, F., and Farzaneh, F. (2011). Synthesis and characterization of brush-like ZnO nanorods using albumen as biotemplate. *Journal of the Brazilian Chemical Society*, *22*(3), 484-488

Okpala, C. C. Nanocomposites–An Overview*International Journal of Engineering Research and Development*, 8(11), 17–23.

Oliveira, M., and Machado, A. V. (2013). Preparation of polymer-based nanocomposites by different routes. *Nanocomposites: Synthesis, Characterization and Applications*, 1-22.

Oskam, G. (2006). Metal oxide nanoparticles: synthesis, characterization and application. *Journal of Sol-Gel Science and Technology*, *37*(3), 161-16

Pal, S. L., Jana, U., Manna, P. K., Mohanta, G. P., and Manavalan, R. (2011). Nanoparticle: An overview of preparation and characterization, *Journal of Applied Pharmaceutical Science* 01(06): 228–34.

Pandya, S. (2007). Nanocomposites and it's application-review

Paques, J. P., van der Linden, E., van Rijn, C. J., and Sagis, L. M. (2014). Preparation methods of alginate nanoparticles. *Advances in Colloid and Interface Science*, *209*, 163-171.

Pholnak, C., Sirisathitkul, C., Suwanboon, S., and Harding, D. J. (2014). Effects of precursor concentration and reaction time on sonochemically synthesized ZnO nanoparticles. *Materials Research*, *17*(2), 405-411.

Polarz, S., Roy, A., Merz, M., Halm, S., Schröder, D., Schneider, L., and Driess, M. (2005). Chemical Vapor Synthesis of Size-Selected zinc oxide nanoparticles. *Small*, *1*(5), 540-552.

Potgieter, J. H., Potgieter-Vermaak, S. S., and Kalibantonga, P. D. (2006). Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, *19*(5), 463-470.

Prado, M. A., Dias, G., Carone, C., Ligabue, R., Dumas, A., Roux, C., and Einloft, S. (2015). Synthetic Ni-talc as filler for producing polyurethane nanocomposites. *Journal of Applied Polymer Science*, *132*(16)

Rahmati, M. M., Rabbani, P., Abdolali, A., and Keshtkar, A. R. (2011). Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae. *Journal of Hazardous Materials*, *185*(1), 401-7.

Raj, A. L. F. A., & Jayalakshmy, E. (2015). Biosynthesis and characterization of zinc oxide nanoparticles using root extract of Zingiber officinale. *Orient J Chem*, *31*, 51-56.

Ramesh, M., Anbuvannan, M., and Viruthagiri, G. (2015). Green synthesis of ZnO nanoparticles using Solanum nigrum leaf extract and their antibacterial activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *136*, 864-870.

Ramimoghadam, D., Hussein, M. Z. B., and Taufiq-Yap, Y. H. (2013). Hydrothermal synthesis of zinc oxide nanoparticles using rice as soft biotemplate. *Chemistry Central Journal*, *7*(1), 1.

Raveendran, P., Fu, J., and Wallen, S. L. (2003).Completely ‘ Green ’ Synthesis and Stabilization of Metal Nanoparticles. *Journal of American Chemical Society,*125(46), 13940–41.

Ravichandran, S., and Karthikeyan, E. (2011). Microwave synthesis-a potential tool for green chemistry. *International Journal of Chem Tech Research*, *3*, 466-470.

Reynolds, J. G., Johnston, C. T., and Agnew, S. F. (2012). A molality-based bet equation for modeling the activity of water sorbed on clay minerals. *Clays and Clay Minerals*, *60*(6), 599-609.

Robati, D. (2013). Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal of Nanostructure in Chemistry*, *3*(1), 1-6.

Roduner, E. (2006). Size matters: why Nanomaterials are different. *Chemical Society Reviews*, *35*(7), 583-592.

Sağ, Y., and Kutsal, T. (2000). Determination of the biosorption activation energies of heavy metal ions on Zoogloea ramigera and Rhizopus arrhizus. *Process Biochemistry*, *35*(8), 801-807.

Sahoo, S., Maiti, M., Ganguly, A., Jacob George, J., and Bhowmick, A. K. (2007). Effect of zinc oxide nanoparticles as cure activator on the properties of natural rubber and nitrile rubber. *Journal of Applied Polymer Science*, *105*(4), 2407-2415.

Salata, O. V. (2004). Applications of nanoparticles in biology and medicine. *Journal of Nanobiotechnology*, *2*(1), 1.

Saleh, T. A. (2016). Nanocomposite of carbon nanotubes/silica nanoparticles and their use for adsorption of Pb (II): from surface properties to sorption mechanism. *Desalination and Water Treatment*, *57*(23), 10730-10744.

Saleh, T. A., Gupta, V. K., and Al-Saadi, A. A. (2013). Adsorption of lead ions from aqueous solution using porous carbon derived from rubber tires: Experimental and computational study. *Journal of Colloid and Interface Science*, *396*, 264-269.

Saleh, T. A., Sarı, A., and Tuzen, M. (2016). Chitosan-modified vermiculite for As (III) adsorption from aqueous solution: Equilibrium, thermodynamic and kinetic studies. *Journal of Molecular Liquids*, *219*, 937-945.

Salehi, R., Arami, M., Mahmoodi, N. M., Bahrami, H., and Khorramfar, S. (2010). Novel biocompatible composite (chitosan–zinc oxide nanoparticle): preparation, characterization and dye adsorption properties. *Colloids and Surfaces B: Biointerfaces*, *80*(1), 86-93.

Samat, N. A., and Nor, R. M. (2013). Sol-Gel synthesis of zinc oxide nanoparticles using citrus aurantifolia extracts. *Ceramics International* 39 ,545–48.

Sarı, A., Tuzen, M., Cıtak, D., and Soylak, M. (2007). Adsorption characteristics of Cu (II) and Pb (II) onto expanded perlite from aqueous solution. *Journal of Hazardous Materials*, *148*(1), 387-394.

Sarier, N., Onder, E., and Ersoy, S. (2010). The modification of Na-montmorillonite by salts of fatty acids: An easy intercalation process. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *371*(1), 40-49.

Seco, A., Gabaldon, C., Marzal, P., and Aucejo, A. (1999). Effect of pH, cation concentration and sorbent concentration on cadmium and copper removal by a granular activated carbon. *Journal of Chemical Technology and Biotechnology*, *74*(9), 911-18.

Şener, S., and Özyılmaz, A. (2010). Adsorption of naphthalene onto sonicated talc from aqueous solutions. *Ultrasonics sonochemistry*, *17*(5), 932-938.

Shah, P., Ramaswamy, A. V., Lazar, K., and Ramaswamy, V. (2004). Synthesis and characterization of tin oxide-modified mesoporous SBA-15 molecular sieves and catalytic activity in trans-esterification reaction. *Applied Catalysis A: General*, *273*(1), 239-248.

Shameli, K., Ahmad, M. B., Al-Mulla, E. A. J., Shabanzadeh, P., and Bagheri, S. (2013). Antibacterial effect of silver nanoparticles on talc composites. *Research on Chemical Intermediates*, 1–13.

Shameli, K., Ahmad, M. B., Yunus, W. M. Z. W., Ibrahim, N. A., and Darroudi, M. (2010). Synthesis and characterization of silver / talc nanocomposites using the wet chemical reduction method. *International Journal of Nanomedicine,* 5, 743–51.

Shankar, S., Teng, X., Li, G., and Rhim, J. W.(2015). Preparation , characterization , and antimicrobial activity of gelatin / ZnO nanocomposite films. *Food Hydrocolloids,* 45, 264–71.

Sharma, D., Rajput, J., Kaith, B. S., Kaur, M., and Sharma, S. (2010). Synthesis of ZnO nanoparticles and study of their antibacterial and antifungal properties. *Thin Solid Films*, *519*(3), 1224-1229.

Sharma, G., Pathania, D., Naushad, M., and Kothiyal, N. C. (2014). Fabrication, characterization and antimicrobial activity of polyaniline Th (IV) tungstomolybdophosphate nanocomposite material: Efficient removal of toxic metal ions from water. *Chemical Engineering Journal*, *251*, 413-421.

Sheela, T., Nayaka, Y. A., Viswanatha, R., Basavanna, S., and Venkatesha, T. G. (2012). Kinetics and thermodynamics studies on the adsorption of Zn (II), Cd (II) and Hg (II) from aqueous solution using zinc oxide nanoparticles. *Powder Technology*, *217*, 163-170.

Sherrington, D. C. (1998). Preparation, structure and morphology of polymer supports. *Chemical Communications*, (21), 2275-2286.

Shimogaki, T., Kawahara, H., Higashihata, M., Ikenoue, H., Nakamura, D., Nakata, Y., and Okada, T. (2015,). Fabrication of ZnO crystals by UV-laser annealing on ZnO nanoparticles prepared by laser ablation method. *International Society for Optics and Photonics*. 93640-93640.

Singh, S., Barick, K. C., and Bahadur, D. (2013). Functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes. *Nanomaterials and Nanotechnology*, 3-20.

Singh, T. S., and Pant, K. K. (2004). Equilibrium, kinetics and thermodynamic studies for adsorption of As (III) on activated alumina. *Separation and purification technology*, *36*(2), 139-147.

Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M., and Mohamad, D. (2015). Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-Micro Letters*, *7*(3), 219-242.

Song, K. C., Lee, S. M., Park, T. S., and Lee, B. S. (2009). Preparation of colloidal silver nanoparticles by chemical reduction method. *Korean Journal of Chemical Engeneering,* 26(1), 153–55.

Soosen Samuel, M., Bose, L., and George, K. C. (2009). Optical properties of ZnO nanoparticles. *Academic Review*, 57-65.

Sprynskyy, M., Kowalkowski, T., Tutu, H., Cukrowska, E. M., and Buszewski, B. (2011). Adsorption Performance of Talc for Uranium Removal from Aqueous Solution. *Chemical Engineering Journal,* 171(3), 1185–93.

Sundarrajan, P., Eswaran, P., Marimuthu, A., Subhadra, L. B., and Kannaiyan, P. (2012). One pot synthesis and characterization of alginate stabilized semiconductor nanoparticles. *Bulletin of the Korean Chemical Society*, *33*(10), 3218-3224.

Talam, S., Karumuri, S. R., and Gunnam, N. (2012). Synthesis, characterization, and spectroscopic properties of ZnO nanoparticles. *ISRN Nanotechnology*

Thareja, R. K., and Shukla, S. (2007). Synthesis and Characterization of Zinc Oxide Nanoparticles by Laser Ablation of zinc in liquid. *Applied Surface Science* 253(22), 8889–95.

Tofighy, M. A., and Mohammadi, T. (2011). Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. *Journal of Hazardous Materials*, *185*(1), 140-147

Torres, A., López de Dicastillo, C., Rios, M., Bastias, I., Guarda, A., and Galotto, M. J. (2014). Effect of organoclay incorporation on thermal, physical and morphological properties of LLDPE nanocomposites for active food packaging applications. *Journal of the Chilean Chemical Society*, *59*(4), 2681-2685.

Trivunac, K., and Stevanovic, S. (2006). Removal of Heavy Metal Ions from Water by Complexation-Assisted Ultrafiltration. *Chemosphere,* 64(3), 486–91.

Tyagi, B., Chudasama, C. D., and Jasra, R. V. (2006). Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *64*(2), 273-278.

Uddin, F. (2008). Clays, nanoclays, and montmorillonite minerals. *Metallurgical and Materials Transactions A*, *39*(12), 2804-2814.

Umer, A., Naveed, S., Ramzan, N., and Rafique, M. S. (2012). Selection of a suitable method for the synthesis of copper nanoparticles. *Nano*, *7*(05), 1230005.

Us Epa O. (2013). National primary drinking water regulations. drink water contaminant 141–2

Vanathi, P., Rajiv, P., Narendhran, S., Rajeshwari, S., Rahman, P. K., and Venckatesh, R. (2014). Biosynthesis and Characterization of phyto mediated zinc oxide nanoparticles, A green chemistry approach. *Materials Letters,* 134, 13–15.

Vaseem, M., Umar, A., and Hahn, Y. B. (2010). ZnO nanoparticles: growth, properties, and applications. *Metal Oxide Nanostructures and their Applications*, *5*, 1-36.

Veli, S., and Alyüz, B. (2007). Adsorption of copper and zinc from aqueous solutions by using natural clay. *Journal of Hazardous Materials,* 149, 226–33.

Vengris, T., Binkien, R., and Sveikauskait, A. (2001). Nickel, copper and zinc removal from waste water by a modified clay sorbent. *Applied Clay Science*, *18*(3), 183-190.

Villaescusa, I., Fiol, N., Martínez, M., Miralles, N., Poch, J., and Serarols, J. (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Research*, *38*(4), 992-1002

Wan, M. W., Kan, C. C., Rogel, B. D., and Dalida, M. L. P. (2010). Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. *Carbohydrate Polymers*, *80*(3), 891-899.

Wang, H. J., Zhou, A. L., Peng, F., Yu, H., & Chen, L. F. (2007). Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb (II) in aqueous solution. *Materials Science and Engineering: A*, *466*(1), 201-206

Wang, J., and Chen, C. (2014). Chitosan-based biosorbents: modification and application for biosorption of heavy metals and radionuclides. *Bioresource Technology*, *160*, 129-141.

Wang, L., and Muhammed, M. (1999). Synthesis of zinc oxide nanoparticles with controlled morphology. *Journal of Materials Chemistry*, *9*(11), 2871-2878.

Wang, S. F., Shen, L., Tong, Y. J., Chen, L., Phang, I. Y., Lim, P. Q., and Liu, T. X.(2005). Biopolymer Chitosan/montmorillonite nanocomposites: preparation and characterization. *Polymer Degradation and Stability,* 90(1), 123–31.

Wang, Y., Li, L., Luo, C., Wang, X., and Duan, H. (2016). Removal of Pb^{2+} from water environment using a novel magnetic chitosan/graphene oxide imprinted Pb^{2+}. *International Journal of Biological Macromolecules*, *86*, 505-511.

Wang, Y., Zhang, L., Tang, C., and Yu, D. (2000). Preparation and characterization of rubber–clay nanocomposites. *Journal of Applied Polymer Science*, *78*(11), 1879-1883.

Wang, Z. L. (2004). Nanostructures of zinc oxide. *Materials Today*, *7*(6), 26-33.

Witek-Krowiak, A., Szafran, R. G., and Modelski, S. (2011). Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination*, *265*(1), 126-134

Wu, Z., Zhou, C., and Zhu, N. (2002). The nucleating effect of montmorillonite on crystallization of nylon 1212/montmorillonite nanocomposite. *Polymer Testing*, *21*(4), 479-483 .

Xu, D., Tan, X. L., Chen, C. L., and Wang, X. K. (2008). Adsorption of Pb (II) from aqueous solution to MX-80 bentonite: effect of pH, ionic strength, foreign ions and temperature. *Applied Clay Science*, *41*(1), 37-46

Xu, P., Zeng, G. M., Huang, D. L., Feng, C. L., Hu, S., Zhao, M. H., and Liu, Z. F. (2012). Use of iron oxide nanomaterials in wastewater treatment: a review. *Science of the Total Environment*, *424*, 1-10.

Yang, H., Du, C., Jin, S., and Tang, A. (2007). Preparation and characterization of SnO 2 nanoparticles incorporated into talc porous materials (TPM). *Materials Letters*, *61*(17), 3736-3739.

Yu, B., Zhang, Y., Shukla, A., Shukla, S. S., and Dorris, K. L. (2000). The removal of heavy metal from aqueous solutions by sawdust adsorption—removal of copper. *Journal of Hazardous Materials*, *80*(1), 33-42.

Yuvakkumar, R., Suresh, J., Nathanael, A. J., Sundrarajan, M., and Hong, S. I .(2014). Novel Green Synthetic Strategy to Prepare ZnO Nanocrystals Using Rambutan (Nephelium Lappaceum L) Peel extract and its santibacterial applications. *Materials Science and Engineering,* 41, 17–27.

Zak, A. K., Razali, R., Majid, W. A., and Darroudi, M. (2011). Synthesis and characterization of a narrow size distribution of zinc oxide nanoparticles. *International journal of Nanomedicine*, *6*, 1399–1403.

Zak, A. K., Abrishami, M. E., Majid, W. A., Yousefi, R., and Hosseini, S. M. (2011). Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol–gel combustion method. *Ceramics International*, *37*(1), 393-398.

Zeng, Q. H., Wang, D. Z., Yu, A. B., and Lu, G. Q. (2002). Synthesis of polymer – montmorillonite nanocomposites by in situ intercalative polymerization. *Nanotechnology* ,13, 549–53.

Zhang, J., Xu, S., Zhang, S., and Du, Z. (2008). Preparation and characterization of tamarind gum/sodium alginate composite gel beads. *Iranian Polymer Journal*, *17*(12), 899-906.

Zhu, X., Yuri, I., Gan, X., Suzuki, I., and Li, G. (2007). Electrochemical study of the effect of nano-zinc oxide on microperoxidase and its application to more sensitive hydrogen peroxide biosensor preparation. *Biosensors and Bioelectronics*, *22*(8), 1600-1604.