

Adsorption of Ni(II) and Fe(II) Ions Using Cross-Linked Modified Chitosan- Khellinone Schiff's Base for Waste Water Treatment

Reham Hassan^{1,2*}, Nehad Abdel Latif^{1,3}, Manal Montasser^{1,4} and Amal H. Abdel-Kader^{1,5}

Assistant Professor, Department of Chemistry, Faculty of Science, Taif university, Saudi Arabia¹

Assistant Professor, Department of Chemistry, Faculty of Science, Helwan University, Cairo, Egypt²

Associate Professor, Department of Natural Compounds Chemistry, Pharmaceutical Industries Division, National Research Center, Cairo, Egypt³

Associate Professor, Department of Central Lab of Pesticides, Agricultural Researches Center, Alexandria, Egypt⁴

Associate Professor, Department of Cellulose and paper, National Research Center, Cairo, Egypt⁵

ABSTRACT: A novel chitosan derivative has been synthesized. The structure and morphology of the new material are characterized by Fourier transform infrared spectroscopy (FTIR) X-ray diffraction (XRD). Chitosan- khellinone Schiff's base was prepared, characterized and successfully applied in the removal of Ni (II) and Fe (II) ions from aqueous real samples. While the metal cations were detected using ICP-OES. The effect of pH (2-9) on the uptake behavior was studied. The optimum initial pH was 6 and 7 for Fe²⁺ and Ni²⁺, respectively. The removal of Ni (II) and Fe (II) from real samples of ground water was applied and the removal efficiency reached to nearly 90%.

KEYWORDS: Chitosan, khellinone Schiff's base, removal of Ni (II), removal of Fe (II), waste water treatment

I. INTRODUCTION

Toxic heavy metal contamination of industrial wastewater is an important environmental problem. Many industries such as electroplating, pigments, metallurgical processes, and mining and leather industries release various concentrations of heavy metals. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese, nickel and iron are commonly detected in both natural and industrial effluents [1]. In spite of strict regulations restricting their careless disposal, these metal cations may still emerge in a variety of wastewaters stemming from catalysts, electrical apparatus, painting and coating, extractive metallurgy, antibacterial, insecticides and fungicides, photography, pyrotechnics, smelting, metal electroplating, fertilizer, mining, pigments, stabilizers, alloy industries, electrical wiring, plumbing, heating, roofing and construction piping, water purification, gasoline additives, cable covering, ammunition and battery industries and sewage sludge [2-4].

In the past few years, special attention has been given to the environmental contamination with heavy metal ions because of their high toxicity and non-biodegradability. The commonly used procedures for removing metal ions from effluents include filtration [5], chemical precipitation [6], chemical coagulation [7], flocculation [8], ion exchange [9], reverse osmosis [10], membrane technologies [11-13] and solvent extraction [14]. However, these methods are limited by high operational cost and/or may also be inefficient in the removal of some toxic metal ions, mainly at trace level concentration [15, 16].

The use of adsorbents of biological and natural origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies. One of the promising methods is the use of chelating resins. Chelating resins are easily regenerated from metal ions and they differ from activated carbon and ion exchange

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

resins in their high selectivity in sorption processes [17]. Many articles that cover a vast number of different chelating resins were reported [18, 19]. Recently, it was reported on the use of magnetic resins in removal of some metals from aqueous solutions [20]. These methods are also cheap and often highly scalable. Attention has recently been focused on natural Schiff's bases and its derivatives as bio-adsorbents. A large number of Schiff bases have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen [21], catalytic activity in hydrogenation of olefins [22] and transfer of an amino group [23], photochromic properties [24], and adsorbing ability towards some toxic metals [25]. The Schiff's base complexes were also tested for antibacterial activity against common pathogenic organisms and showed mild to moderate activity [26].

Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively [27]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [28]. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal; agrochemical and biological activities [29,30]. With the increasing incidence of deep mycosis there has been increasing emphasis on the screening of new and more effective antimicrobial drugs with low toxicity. Schiff base complexes are considered to be among the most important stereo-chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [31]. A considerable number of Schiff base complexes have potential biological interest, being used as more or less successful models of biological compounds [32]. They played a seminal role in the development of modern coordination chemistry as well as they can be found at key points in the development of inorganic biochemistry, catalysis and optical materials [33].

Chitosan is a linear natural polymer, produced usually by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.). Due to its structure containing many functional groups as amine or hydroxyl [34]. The major use of chitosan is to purify wastewaters. At present, people are growing concerned that heavy metals, insecticides and their accumulations in food chains will cause ecological damages and health hazard. Therefore, wastewater is required to be treated before discharge. Amino group in chitosan can form a coordinate-covalent bond with metal ion. As a result, chitosan has been widely applied in waste-water treatment. Chitosan exhibits excellent properties in collecting heavy metal ions [35]. Amino group and hydroxyl group in chitosan molecular can react with metal ions, such as Hg^{2+} , Cu^{2+} and Zn^{2+} , to form stable chelates [36, 37], and effectively remove toxic heavy metal ions from industrial wastewaters [36]. Therefore, application of chitosan has been of great significance in environmental protection.

In the present work, a novel chitosan derivative was prepared by reacting the amine group of chitosan with the carbonyl group present in khellinone to yield chitosan- khellinone Schiff's base. The newly synthesized compound was characterized by fourier transform infrared (FTIR). Also the new Schiff base derivative was evaluated by X-ray diffraction (XRD). The effect of pH on the removal was investigated.

II. RELATED WORK

The contamination of water resources with heavy metals is a serious environmental problem, due to the fact that heavy metals are highly toxic at low concentrations, and accumulate in living organisms, which cause many disorders and diseases and serious problems for human health and wildlife. And so it was necessary to remove or reduce the concentration of heavy metals in aquatic systems, and usually apply various methods and technologies in the treatment of contaminated water, these methods include precipitation, ion exchange, and filtration operations. However, the application of some of these methods may be impractical because of economic constraints, or may be insufficient and ineffective in removing some of the toxic metal ions, especially in tracking the level of low concentrations. Some heavy metals, especially copper, zinc and chromium in small quantities are necessary for a healthy life for humans, but most of the heavy metals, including nickel, iron and other causes often in cases of human poisoning and environmental pollution in general. Since these metals have the ability to blend into the water they may seep into the groundwater and thus contaminated drinking water and then harm the consumer of this contaminated water. He

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

therefore called this recent legislation and principles aquatic environment as well as the attention of scientists and researchers all over the world to get to many of the modern techniques and technologies to address the heavy metal pollution . With the increasing demand for water , the environment and safety laws have become more stringent and has developed more in research efforts to improve water treatment processes and among these methods way . Such as the selective adsorption of biological materials , metal oxides , activated carbon, or polymer resins . For interested scientists devise new ways describes the basic technologies available for the removal of heavy metals in the water. As the current methods used to get rid of heavy metals such as chemical processing plant , or currently have a dynamic of their pros and cons. This led scientists to trace the concentration of heavy metals and toxic elements in different samples . These studies aimed at several targets , including a proposal safe and economical ways to address integrated water contaminated tremendous benefit to public health and be economically and environmentally friendly

III. EXPERIMENTAL

II.1. Materials. All reagent used were of Analytical Reagent Grade stated. Sodium hydroxide and nitric acid (69%) were purchased from Avonchem (UK) and Sigma-Aldrich (Germany), respectively. De-ionized water with conductivity $<0.2 \mu\text{S}/\text{cm}$ obtained from a Milli-Q water system (Millipore, France, Elix 10) was used to prepare standard samples, dilute samples and washing all glassware throughout. Mixed working standard solutions of the investigated mineral and toxic heavy metal ions were prepared by appropriate stepwise dilutions of certified stock atomic spectroscopy standards (5% HNO_3 , 3-500 mg kg^{-1} , Perkin Elmer, USA) were used for ICP-AES validation measurements. Khellin and Ethylamin were purchased from Sigma-Aldrich (Germany).

II.2. Apparatus. In the characterization of the prepared Schiff base, the melting points measurements were taken in electro thermal capillary melting points apparatus and are uncorrected. Infrared spectra (ν, cm^{-1}) was recorded on Jasco FT-IR 4100 instruments using KBr Disks, Micro analytical center ,Cairo University, Cairo, Egypt. The prepared derivative was characterized by X-ray diffraction (XRD) technique using an X-ray diffractometer (Bruker Germany, D8 Advance, 2.2 KW Cu Anode, (Ceramic X-ray) with $\text{CuK}\alpha$ radiation ($k = 1.5406 \text{ \AA}$).

II.3. Methods : Preparation of Chitosan-benzofuran Derivative. In a beaker dissolve 10g of benzofuran derivative in 400 mL ethanol absolute. In a separate beaker dissolve 12 g of low molecular weight chitosan in 400 mL distilled water containing 8 mL conc acetic acid and stir at 40°C till complete dissolution. Mix the two beakers to each other gradually and under stirring.

Metal detection:. The Ni(II) and Fe(II) ions were analyzed using ICP-OES under optimized plasma condition. Using the auto-sampler, the measured samples were nebulized downstream to the plasma and the concentrations were automatically determined using the standard calibration graph. The system was adjusted to measure the samples in triplicates and the relative standard deviation was automatically calculated. The RSD was $< 2 \%$ and the correlation coefficient was > 0.99998 .

The adsorption behavior of the Chitosan-Schiff base toward Ni(II) and Fe(II)ions.

Real samples applications: Aliquots of collected from Taif City were used as real samples in this study. The effect of pH on the adsorption behavior of the prepared Chitosan-benzofuran derivative towards Ni(II) and Fe(II) ions were determined. The Ni(II) and Fe(II) concentration of the samples was measured before and after treatment. The removal percent was then calculated. In the effect of pH studies, the uptake experiments were performed at controlled pH and at room temperature by shaking 0.05 g of dry Chitosan-Schiff base with 10 mL of real sample of different pH values (2-9) for 2hours at 150 rpm. The pH of the solutions was adjusted using suitable buffers.

In all batch sorption studies, the percentage of metal ion removal was evaluated from the equation [38]:

$$\% \text{ Removal} = [(C_0 - C_e) / C_0] * 100 \dots\dots\dots(1)$$

Where, C_0 is the initial metal ion concentration and C_e is the metal ion concentration at equilibrium.

IV. RESULTS AND DISCUSSION

III.1. FTIR Spectra

Fig. 1 a,b shows the FTIR spectra of chitosan and chitosan- benzofuran derivative, respectively. The pure chitosan spectrum in Figure 1a shows several characteristic peaks at 3360, 2919, 2874, 1640, 1592, 1375, 1153, 1061 and 893 cm^{-1} [39]. The characteristic peak's assignment of the chitosan- benzofuran derivative (Figure 1b) at 1632 cm^{-1} is due to Schiff base (C=N) formed by a cross linking reaction between the amino group and the ketonic group of khellinone, 3430 cm^{-1} (O-H group of chitosan), 2924 and 2858 cm^{-1} (C-H stretching), 1528 cm^{-1} (C=C stretching of aromatic ring)

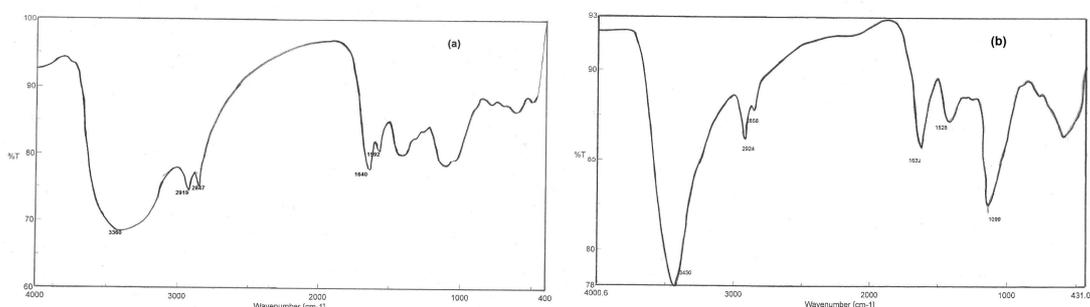


Figure 1: Fourier transform infrared (FT-IR) spectra of pure chitosan (a) and chitosan- benzofuran derivative (b).

III.2. X-ray Diffraction (XRD) Study

Fig. 2 a,b show the X-ray diffraction patterns of the studied chitosan in both cases pure and treated . Study of crystalline phase was determined by the X-ray diffraction (XRD) using Philips equipment type PW, 1710 provided with a copper target and nickel filter. It is clearly observed from Fig. (2a) that pure chitosan exhibit very broad two crystal peaks that appeared at $2\theta = 12^\circ$ and $2\theta = 21^\circ$. On the other hand, the treated chitosan displayed two weak peaks at $2\theta = 22^\circ$ and at $2\theta = 33^\circ$. The broad peaks for pure chitosan which observed at $2\theta = 12^\circ$ disappeared in compound chitosan- benzofuran derivative, while the very broad peak at $2\theta = 21^\circ$ of pure chitosan become weak in chitosan- benzofuran derivative [40].

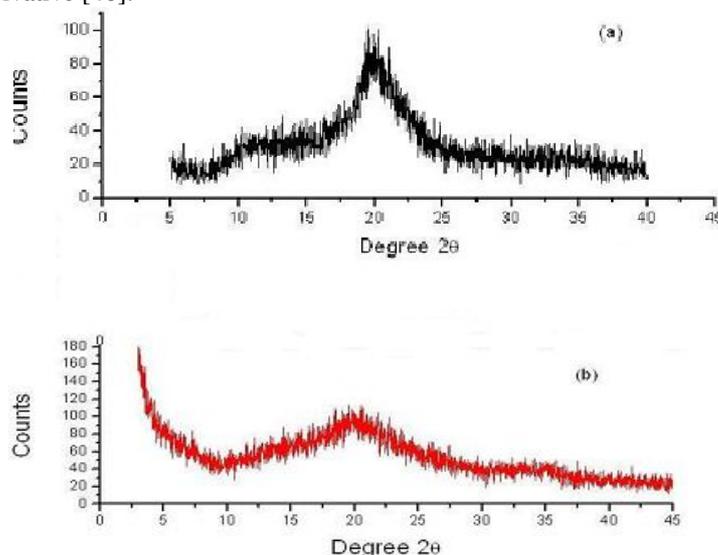


Figure 2: X-ray Diffraction (XRD) pattern of pure chitosan (a) and chitosan- benzofuran derivative (b).

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

These results suggest that chitosan has good compatibility, which leads to the formation of a porous xerogel network. On the other hand, the X-ray diffraction patterns of chitosan- benzofuran derivative displays an amorphous (non-crystalline form).

III.3. The adsorption behavior studies of Chitosan-Schiff base towards Ni(II) and Fe(II) ions.

The effect of pH of the metal ion test solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions, on the functional groups of the adsorbent and the degree of ionization of the adsorbent [38]. To examine the effect of pH on metal ions removal efficiency, the pH was varied from 2.0 to 9.0 for Ni(II) and Fe(II) and the pH of the solutions was adjusted to different values using suitable buffers. The concentrations of Ni(II) and Fe(II) in the different solutions were properly determined directly before and after shaking the mixture for 2h.

The removal efficiency was calculated and the results obtained were represented in Fig. 3. The data was shown that, the uptake of free ionic Ni(II) and Fe(II) depend greatly on pH, where optimal metal removal efficiency. The pH values selected in the experiments were prior to the precipitation limit of each metal ion (pH 6 and 7 for Fe²⁺ and Ni²⁺, respectively) [41]. As shown in Fig.3, the higher uptake capacity was achieved at higher pH values. The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active groups [42]. This behavior is expected, as the acidity of the medium can affect the metal uptake on the natural sorbent because hydrogen ions could compete with metallic ions for active sites on the natural sorbent surface. Also at low pH, most of the active functional groups in the resin were ionized and presented in the protonated positively charged form, electrostatic repulsion between the metal cations and the protonated groups may prevent the adsorption of the metal ions onto the resin [43]. At pH > 7 the metal ion retention become nearly stable because small amount of metal cations started to deposit as hydroxides. This also supports the chelation of the cations on the resin.

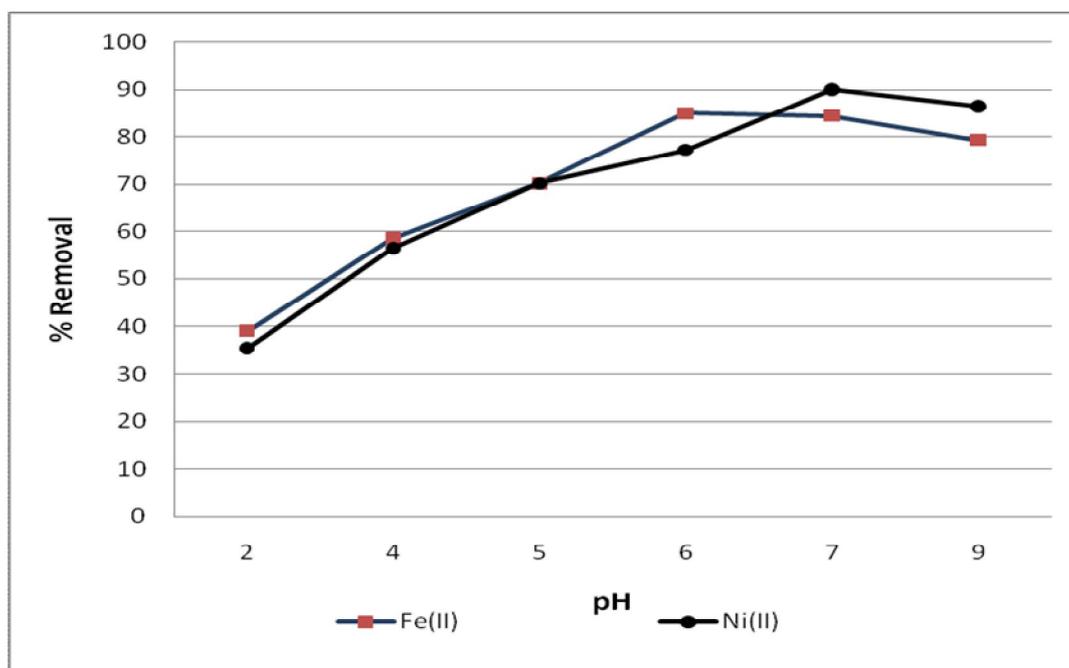


Figure 3: Effect of the pH on the removal of Ni(II) and Fe(II) ion using Chitosan-Schiff base.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

IV. CONCLUSION

In conclusion, a Chitosan- khellinone Schiff's base was prepared, characterized (by means of FTIR and XRD, and successfully applied in the removal of Ni(II) and Fe(II) ions from aqueous real samples using ICP-OES . The results include studying the effect of pH on the uptake behavior in order to select the optimum pH for the removal of Ni(II) and Fe(II) from real samples of ground water from Taif city and we find that the removal efficiency reached to nearly 90%.

V. ACKNOWLEDGMENT

The authors is gratefully acknowledge Taif University, Saudi Arabia for financial support of this project under contract No. 3232-435-1

REFERENCES

- [1] El-Sayed, G.O., H. A. Dessouki and S. S. Ibrahim.. "Removal of Zn(II), Cd(II) and Mn(II) from aqueous solutions by adsorption on maize stalks". The Malaysian Journal of Analytical Sciences, Vol 15 No 1 ,pp. 8 – 21,2011.
- [2] Kocaoba, S.and T. Akyuz.. "Effects of conditioning of sepiolite prior to cobalt and nickel removal". Desalination,Vol. 181,pp. 313-318, 2005 j
- [3] Wu, F.C., R.L.Teseng and R.S. Juang.. "Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan". Water Res.,Vol. 35,pp. 613-618, 2001.
- [4] Zhoua, L., Y. wang, Z. Liu and Q. Huang.. "Characteristics of equilibrium, kinetics studies for adsorption of Hg (II), Cu (II) and Ni (II) ions by thiourea-modified magnetic chitosan microspheres". J. Hazared. Mater.,Vol.161,pp. 995-1002, 2009.
- [5] Bessbousse, H., Rhlalou, T., J.F. Verchère and L. Lebrun.. "Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly (ethyleneimine) in a poly (vinyl alcohol) matrix". Journal of Membrane Science,Vol. 307,pp. 249-259, 2008.
- [6] Esalah, J.O., M.E. Weber and J.H. Vera.. "Removal of lead from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate". Separation and Purification Technology, Vol.18,pp. 25-36,2000.
- [7] El Samrani, A.G., B.S. Lartige and F. Villieras.. "Chemical coagulationof combined sewer over flow: heavy metal removal and treatment optimization". Water Research, Vol.42,pp. 951-960, 2008.
- [8] Ofir, E., Y. Oren and A. Adin.. "Comparing pretreatment by iron of electro-flocculation and chemical flocculation". Desalination, Vol.204,pp. 87-93, 2007.
- [9] Lin, L.-C., J.K. Li and R.S. Juang.. "Removal of Cu (II) and Ni (II) from aqueous solutions using batch and fixed-bed ion exchange processes". Desalination,Vol. 225,pp. 249-259, 2008.
- [10] Benito, Y. and M.L. Ruiz.. "Reverse osmosis applied to metal finishing wastewater". Desalination,Vol. 142,pp. 229-234,2002.
- [11] Cooper, C.A., Y.S. Lin and M. Gonzalez. 2004. "Separation properties of surface modified silica supported liquid membranes for divalent metal removal/recovery". Journal of Membrane Science,Vol. 229,pp. 11-25,2004.
- [12] Juang, R.S. and R.C. Shiau.. "Metal removal from aqueous solutions using chitosan-enhanced membrane filtration". Journal of Membrane Science, Vol.165,pp. 159-167, 2000.
- [13] Nasef, M.M. and A.H. Yahaya.. "Adsorption of some heavy metal ions from aqueous solutions on Nafion 117 membrane". Desalination,Vol. 249,pp. 677-681,2009.
- [14] Gupta, S.K., N.S. Rathore , J.V. Sonawane , A.K. Pabby , P. Janardan , R.D. Changrani and P.K. Dey.. "Dispersion-free solvent extraction of U(VI) in macro amount from nitric acid solutions using hollow fiber contactor". Journal of Membrane Science, Vol.300,pp. 131-136, 2007.
- [15] Yurdakoc, M., Y. Scki and S.K. Yuedakoc.. " Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40 and Siral 80". J. Colloid Interf. Sci. Vol.286,pp. 440-446,2005.
- [16] Monier, M., D.M. Ayad and A.A. Sarhan.. "Adsorption of Cu (II), Hg (II) and Ni (II) ions by modified natural wool chelating fibers". J. Hazared. Mater. Vol.176,pp. 348-355,2010.
- [17] Donia, A.M., A.A. Atia and K.Z. Elwakeel.. "Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde". J. Hazared. Mater. Vol.151,pp.372-379,2008.
- [18] Wan, L., Y. Wang and S. Qian, "Study on the adsorption properties of novel crown ether cross-linked chitosan for metal ions". J. Appl. Polym. Sci.,Vol. 84,pp.29-34,2002.
- [19] Varma, A.J., S.V. Deshpande and J.F. Kennedy., "Metal complexation by chitosan and its derivatives: a review". Carbohydr. Polym Vol. 55,pp.77-93,2004.
- [20] Donia, A.M., A.A. Atia and K.Z. Elwakeel., "Selective separation of mercury (II) using a synthetic resin containing amine and mercaptan as chelating groups". React. Funct. Polym.,Vol. 65pp.267-275,2005.
- [21] Sans, D., A. Perona, R.M. Claramunt and J. Elquero , "Synthesis and spectroscopic properties of Schiff bases derived from 3-hydroxy-4-pyridinecarboxaldehyde".Tetrahedron Vol.61,pp. 145-154,2005.
- [22] Olie, G.H. and S. Olive. , "The Chemistry of the Catalyzes Hydrogenation of Carbon Monoxide". Springer, Berlin ,Vol. 152,pp.301-315, 1984.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 6, June 2015

- [23] Curini, A., F. Epifano, F. Maltese and M.C. Marcotullio. 2002. "Novel chiral Schiff base ligands from amino acid amides and salicylaldehyde". *Tetrahedron Lett.*, Vol. 43, pp. 3821-3823, 2002.
- [24] Taha, N. E. , "Synthesis, Characterization, Photophysical and Computational Study of Schiff Base Ligands and Their Zn (II) Complexes". Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy University Sains Malaysia, 2009.
- [25] Monier, M. , "Adsorption of Hg²⁺, Cu²⁺ and Zn²⁺ ions from aqueous solution using formaldehyde cross-linked modified chitosan-thioglyceraldehyde schiff's base". *International Journal of biological macromolecules*, Vol.50, pp. 773-78, 2012.
- [26] Hindy, A. M. , "Metal Complexes of Schiff Bases: Preparation, Characterization, and Biological Activity". *Turk J Chem.*, Vol.30, pp. 361 – 382, 2006.
- [27] Yarows, S.A., Fusilier, W.E. and Weder, A.B. , "Sodium concentration of water from softeners". *Archives of Internal Medicine*; Vol.157, no.2, pp.218–22, 1997.
- [28] Das, G. and Janine, F. , "The effects of home water softeners: added sodium may be hazardous to your health". *Journal of Environmental Health*; Vol. 50, no.7, pp.1500-1510, 1980.
- [29] Das, G. , "You and your drinking water: health implication for the use of cation exchange water softeners". *Journal of Clinical Pharmacology*; Vol.28 pp.683–90, 1988.
- [30] He, F.J. and MacGregor, G.A. , "Effect of modest salt reduction on blood pressure: a meta-analysis of randomized trials". Implications for public health. *Journal of Human Hypertension*; Vol.16 pp.761–770, 2012.
- [31] Du Cailar, G., Ribstein, J. and Mimran, A. , "Dietary sodium and target organ damage in essential hypertension". *American Journal of Hypertension*; Vol.15, pp.222–229, 2002.
- [32] Ghizellaoui, S., Chibani, A. and Ghizellaoui, S. , "Use of nanofiltration for partial softening of very hard water". *Desalination*; Vol.179, pp.315–322, 2005.
- [33] Gabrielli, C., Maurin, G., Francychausson, H., Thery, P., Tran, T. and Tlili, M. , "Electrochemical water softening: principle and application". *Desalination*; Vol. 201, pp.150–163, 2006.
- [34] Ma, G., D. Yang, J.F. Kennedy and J. Nie.. "Synthesize and characterization of organic-soluble acylated chitosan". *Carbohydrate Polymers*, Vol.75 pp. 390-394, 2008.
- [35] Jeon, C. and K. H. Park.. "Adsorption and desorption characteristics of mercury ions using aminated chitosan bead". *Water Res*, Vol. 39, no.16, pp. 3938-3944, 2005.
- [36] Guibal, E., N. Von Offenbergen Sweeney and T. Vincent.. "Sulfur derivatives of chitosan for palladium sorption. *Reactive & Functional Polymers*", Vol.50, no.2, pp. 149-163, 2002.
- [37] Ruiz M, Sastre A M & Guibal E.. "Palladium sorption on glutaraldehyde-crosslinked chitosan. *Reactive & Functional Polymers*", Vol.45 no.3, pp. 155-173, 2000.
- [38] Morliere, P., H. Honigsmann, D. Averbeck, M. Dardalhon, G. Huppe, B. Ortel, R. Santus and L. Dubertret. 1988. *J. Invest. Dermatol.* 90 : 720.
- [38] Choi, K.J.S., Kim, G., Kim, C.W. and Park, J.K. , "Removal efficiencies of endocrine disrupting chemicals by coagulation/flocculation, ozonation, powdered/ granular activated carbon adsorption, and chlorination". *Korean J. Chem. Eng.*, Vol.23, pp.399–408, 2006.
- [39] Kumar, S., J. Koh, H. Kim, M.K. Gupta and P.K. Dutta., "A new chitosan-thymine conjugate: Synthesis, characterization and biological activity". *Int. J. Biol. Macromol.*, Vol. 50, pp. 493–502, 2012.
- [40] Norton, F. H. 1970. "Fine ceramics technology and applications", McGraw-Hill Book Company, New York, 1970.
- [41] Zhoua, L., Y. Wang, Z. Liu and Q. Huang. , "Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II) and Ni(II) ions by thiourea-modified magnetic chitosan microspheres". *J. Hazard. Mater.*, Vol. 161, pp.995-1002.
- [42] Rosenberg, D.M., McCully, P. and Pringle, C.M. , "Global-scale environmental effects of hydrological alterations: introduction". *BioScience* , Vol.50, pp. 746–751, 2000.
- [43] Monier, M., D.M. Ayad, Y. Wei and A.A. Sarhan. , "Adsorption of Cu(II), Co(II), and Ni(II) ions by modified magnetic chitosan chelating resin". *J. Hazard. Mater.*, Vol. 177, pp. 962- 970, 2010.