

Chitosan based chemical sensors for determination of mercury in water: a review

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Abstract. This manuscript briefly reviews several researches on mercury pollution, chitosan as the advance material and mercury sensor fabricated from chitosan based materials. Chitosan is a natural polymer that has structure analogue to cellulose. It contains many functional groups that provide binding sites for metal ions including mercury ions. Chitosan could stabilize gold and silver nanoparticles and the presence of mercury ion affected on the particle arrangement. The intensity of nanoparticle spectra decrease gradually with increasing the concentration of mercury ions.

Key Words: polymer, pollution, fish, nanoparticles, colorimetric.

Introduction. Chitosan is a natural polymer converted from chitin that is isolated mainly from exoskeleton of crustacean especially shrimps, although chitosan can also be isolated from fungi (Dhillon et al 2013). Isolation process involved several steps including extraction and isolation of chitin, demineralization and deacetylation (Paul et al 2014). Chitosan has been widely used (Rinaudo 2006) and commercially applied in many fields including the utilities on nanomaterial preparations (Shukla et al 2013). Chitosan has a structure analogue to cellulose but there is amino group at each polymer chains as shown in Figure 1.

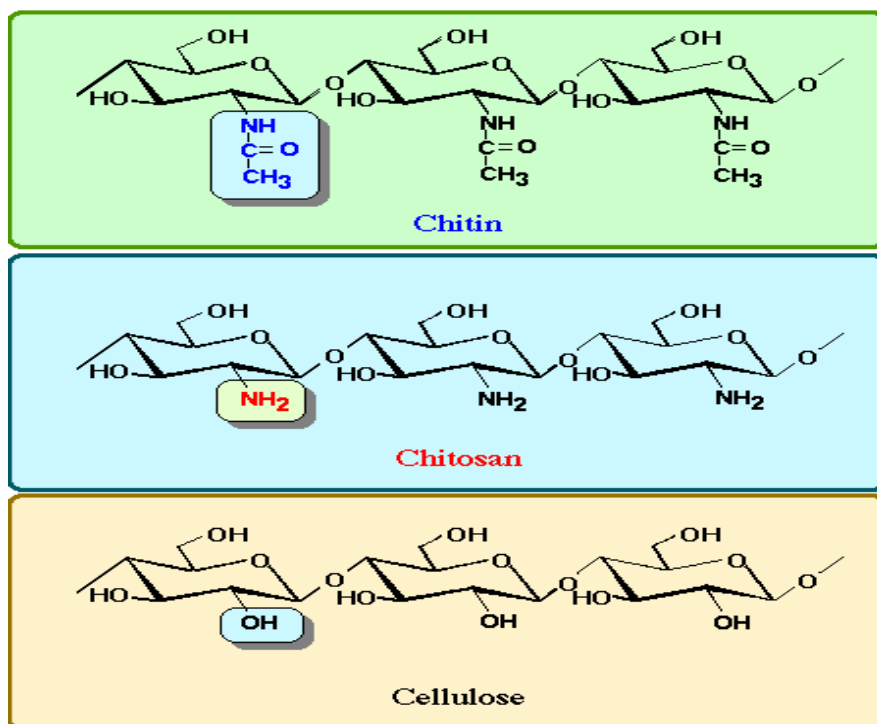


Figure 1. Comparison chemical structure of chitin, chitosan, and cellulose (<http://dalwoo.tripod.com/structure.gif>).

Naturally mercury (Hg) occurs in earth' crust and it releases to environments by volcanic eruption, weathering of rock and as result of human activity. Mercury has been world widely reported as food and drinking water contamination. The toxicity level of mercury depends on the species; elemental, inorganic and organic mercury (Du et al 2015). Although it was reported was mainly in laboratory set up, elemental mercury can be oxidized to form ionic (inorganic mercury) and mercury ion in appropriated condition can be transformed by bacteria to organic mercury compounds including mono- and dimethylmercury which is highly toxic for human.

Mercury determination is crucial, however it is required sophisticated and expensive analytical equipment such Atomic Absorption Spectrometer (AAS), Induced Couple Plasma (ICP) etc. Recently many studies have been reported on mercury sensor fabrication. This paper aims to reviews those but it focuses on chitosan based sensor.

Resource of mercury pollution in water. Mercury pollution comes from many resources, the larger source was from power plant which is around 33 tones mercury pollution in US annually (NRDC 2000). The average mercury content in coal was 395 ng per gram of coal (Yuan et al 2010). The power plant uses coal containing mercury as the energy and the mercury release to environment during combustion. The second source was gold mining that are around 10-20 million miners in the world. Every 1 g of gold extracted with amalgamation process, it released 1.2-1.5 g of mercury to environment. Typically 3-4 tones mercury lost in Tanzania and 4 tones in Zimbabwe annually (Van Straaten 2000). Other mercury pollution sources were from manufacturing metals and cements through smelting process. Other industrial mercury emitter including chlor-alkali and poly vinyl chloride (PVC) industries release mercury as waste from the chemical process. Fuel burning and consumer product industries such as thermometer, batteries, electronic device and many automotive parts also gave significant amount of mercury pollution through incineration of the waste (NRDC 2000).

Mercury is present in various forms, most are inorganic salt trapped in coal, rock and sediment. Other was as elemental mercury that is used in gold mining and polluting environment by burning or heating the gold-amalgam and tailing from amalgamation process. Elemental mercury and most of inorganic salt except the nitrate compounds are insoluble in water. One tone of elemental mercury will only dissolve 0.06 g in water (Clever et al 1985). However, by heating the inorganic salt that occur naturally in volcano eruption, geothermal plant or in industries, gas mining, burning coal and fuel as well as gold mining, more soluble compounds might form. More than 90% of mercury in surface water comes from atmospheric deposition (Leopold et al 2010). The surface water distributes the compounds into food chain. The elemental mercury which is also insoluble in water, is oxidized to Hg(II) at certain condition and slowly dissolved in water. Dissolved mercury can be absorbed by algae, micro- and macro-invertebrate and fish (diFrancesco & Shinn 2002).

The solubility of elemental mercury (Hg^0) was studied by Amyot et al (2005) by doing simulation in laboratory. They dissolved elemental mercury in water containing different concentration of oxygen (hypoxic and saturated condition, chloride ions (0, 5 and 500 micro molar) and hydrogen ions (at pH 5 and 7). The dissolved mercury and total mercury was monitored from 2 to 6 h. The author reported that elemental mercury was not rapidly oxidized by oxygen and chloride and this finding was in contrast with earlier studies in the same condition reported by Magalhães & Tubino (1995), and Yamamoto (1996). Soaking elemental mercury in water and in darkness affected more on the oxidation process rather than the solubility. Oxidation rate increased 3 fold in the presence of chloride ion. The initial oxidation rate was slightly affected by the presence of dissolved oxygen but it was slower at the saturated oxygen condition. The total concentration of dissolved mercury from 0.1 mL of Hg^0 in 100 mL water was only 68 mM with half-live of 30 years or it takes 30 years to dissolve 0.05 mL. However in oxygenated sea water, the half-life reduced to 5 years if the initial rate of the oxidation is maintained constant (Amyot et al 2005).

Changing mercury Hg(II) ions into mono methylmercury (MMeHg) and dimethylmercury (DMHg) is most concerned and has been discussed continuously. Methyl mercury has reputation as a neurotoxic compound since it has high affinity to thiol group in protein structure and analogical poison in Minamata mercury pollution. Although in Minamata case methylmercury formed chemically in a reactor as a side product from synthesis of aldehyde, study on natural process which later known as biomethylation was also reported (Wood et al 1968). Biomethylation is a process of living organism to produce a direct linkage a methyl group (CH₃-) to the metal or metalloid. Biomethylation of CH₃-Hg or MMeHg was reported mainly in sediment and anaerobic bacteria are believed as the main agent of biomethylation (Craig & Jenkins 2004; Schaefer & Morel 2009). Schaefer et al (2011) used bacteria of FeRB *Geobacter sulfurreducens* and the SRB *Desulfovibrio desulfuricans* ND132 as model for biomethylation host, and using thiol compounds as the active transport for Hg(II) into the bacteria. They reported that Hg (II) uptake was higher in *D. desulfuricans* than in *G. sulfurreducens*. Complexation between Hg(II) and thiols was the important factor for controlling Hg methylation in anaerobic environment (Yamamoto 1995). Almost all of biomethylation experiments were used mercury salt rather than elemental mercury, probably because the salt has higher solubility than the elemental one. Model of mercury species transformation was written by Leopold et al (2010).

Mercury pollution in fish. The mercury contamination in fish has been studied intensively since 1974. Predatory fish from Willard Bay Reservoir, Utah, has 1.5-7.3 mg kg⁻¹ wet weight mercury in their flesh especially in large-mouth-bass fish (*Micropterus salmoides*) and this concentration was very much higher than those from the reference area that was only 0.040-0.820 mg kg⁻¹ wet weight (Smith et al 1974 in Stokes & Wren 1987). In Willard Bay, it was found high mercury pollution naturally. It might come from insoluble mercury salt and sulfides from surrounding. Large-mouth-bass fish accumulated mercury in the tissue and it was also biomagnified through the aquatic food chain. Abernathy & Cumbie (1977) reported elevated mercury level in large-mouth-bass fish although the water contained low mercury concentration. They also reported that mercury level in bass flesh increased with growing the age.

Mercury polluted fish was reported over the world, in rivers in the North of Luxembourg, the level was 10.3 and 534.5 ng g⁻¹ wet weight (Boscher et al 2010), in Canadian Arctic was 500-1000 ng g⁻¹ (Scheuhammer et al 2015) and in Caspian lake, Iran was up to 840 ng L⁻¹ (Sari et al 1981 cited in Azimi & Sadeghi Moghaddam 2013). This level is beyond the maximum allowable mercury contents for commercial fish that is 500 ng g⁻¹ for shipments exported to the United States markets. Standard for maximum allowable uptake of methyl mercury in human diet was 1.6 µg kg⁻¹ body weight per week recommended by World Health Organization (WHO) and 0.1 µg kg⁻¹ body weight per day for adult was stated by the United States Environmental Protection Agency (EPA) and National Research Council (NRC) (FAO/WHO 2003; NRDC 2000).

The level of mercury uptake by fish was affected the water quality. In hard water (containing CaCO₃ of 385 mg L⁻¹) was found less mercury than in soft water (containing CaCO₃ of 30 mg L⁻¹) (Rodgers 1982). The authors suggested that anaerobic conditions in the more nutrient-rich systems would result in binding of mercury to sulfur compounds and organics, which would remove the mercury from the food web.

Determination of mercury species. Mercury exists in many forms; as insoluble salts (HgS, HgCO₃), dissolved mercury (Hg²⁺, Hg₂²⁺ and its complexes), elemental liquid mercury (Hg⁰), mercury vapor (elemental mercury in gas phase, Hg⁰), and organomercury (R-Hg) including mono and dimethyl mercury (MMeHg, DMeHg); These variations are known as mercury species (Hauserova et al 2006). The mercury vapor might be found in air in short time, it can be detected as gas using mercury vapor analyzer or trapped in KMnO₄ solution and analyzed with Atomic Absorption Spectrophotometer (AAS) as dissolved mercury (Prokopowicz & Mniszek 2005). Dissolved and MMeHg can be found in fresh water that are complexed with dissolved hummic

matter but DMeHg is more lightly found in sea water rather in fresh water (Hudson et al 1994; Mason & Fitzgerald 1991).

The elemental mercury and the insoluble salts are usually deposited in the bottom of water (Kotnik et al 2007). Most of mercury analysis and common determination were on the total mercury concentration (Da Silva et al 2014; Bansal et al 2014; Panichev & Panicheva 2015; Mandjukov et al 2015; D'Agostino et al 2014; Ernowati 2014). While detection of mercury species is challenging since it is trace element (nano gram) and some are volatile. Often it is required pre-treatment by extraction and chromatographic separation, prior to mercury detection, pre-concentration and then analyze with high-tech and expensive instrument as shown in Table 1 cited from Leopold et al (2010). The separation section is usually performed using Gas chromatography (GC), High Performance Liquid Chromatography (HPLC), capillary electrophoresis and others as reviewed by Leopold et al (2010). The detection equipments are Inductively Couple Plasma Atomic Emission Spectrophotometry (ICP-AES), Microwave Induced Plasma AES (MIP-AES), ICP-mass spectrometry (ICP-MS) or Atomic Fluorescence Spectrometry (AFS), etc (Leopold et al 2010; Niazi et al 2015; Li et al 2015; Qazi et al 2012).

The simple mercury detection technique was reported by Maršálek & Svobodová (2006). They determined methylmercury in fish tissue by using technique of gas chromatography (GC) with a DB-608 capillary column and Electron Capture Detector. The heating programmed was hold 2 min at 140°C, gradient 4°C/min to 160°C; hold 2 min at 160°C; injector temperature (240°C), detector temperature (300°C). Prior to analysis the sample was acidic digestion and extracted with toluene, then centrifuged and cooled at 4°C. MMeHg peak retention time was 4.5–4.9 min depending on the condition of the column. The standard solution for methyl mercury was methylmercury chloride in isoctane. They reported that detection limit was 13 µg kg⁻¹ and reproducibility was 9.4%.

Table 1

General process for mercury determination (Leopold et al 2010)

<i>Pre-treatment</i>	<i>Pre-concentration</i>	<i>Separation</i>	<i>Detection/Quantification</i>
Extraction (liquid/liquid; solid phase micro-extraction)	Solid phase microextraction	High performance Liquid chromatography Gas chromatography	Inductively coupled plasma atomic emission spectrometry Microwave induced plasma atomic emission spectrometry
Derivatisation (hydride generation, alkylation) Cold vapor generation (chemical; ultrasound)	Amalgamation	Capillary electrophoresis	Inductively coupled plasma mass spectrometry Inductively coupled plasma isotope dilution mass spectrometry
Distillation (selective) Reduction (selective) Decomposition Complexation	Cryo trapping	Non chromatographic techniques based physical/chemical differences	Atomic fluorescence spectrometry Quartz furnace atomic absorption spectrometry Graphite furnace atomic absorption spectrometry

Chemical sensor. Sensor is commonly defined as a device that receives and responds to the signal or stimulus. The device is combination of sensitive components which give the respond or stimulus is in form of or is converted into electrical signal (Fraden 2010). Another sensor definition was stated by Stetter et al (2003); sensor is “a small device that as the result of a chemical interaction or process between the analyte gas and the sensor device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal”. A special branch of chemical sensor is

biosensor for recognition of biochemicals and bio-reactions (Sekhar et al 2010). Sensor converts any type of energy to electrical signal while transducer converts one type of energy to another. Actuator may be described opposite to sensor, it converts electrical signal to generally nonelectrical energy and transducer is component of a complex sensor (Fraden 2010). Chemical sensor involves chemical reaction either as stimulus or respond. Typically a transducer converts chemical reaction into heat and another part, thermopile which converts heat into electrical signal.

Generally, concentration of ions or compound was determined using sophisticated analytical instrument such AAS, ICP, GC, HPLC, UV-Vis Spectrophotometer etc. It is high accuracy but most are expensive instrument, large in size and required skillful operator and time consuming. Sensor is miniaturized the large equipment, portable and low cost. However it often has problem with the sensitivity, selectivity, base line stability and reproducibility (Fraden 2010).

According to transduction, chemical sensor was group in three classes that are (1) sensor that measures the electrical or electrochemical properties; (2) sensor that measures a change in physical properties; (3) sensor that responds the optical absorption. Some sensors are not easily to be classified since they work based on combination of physical and chemical properties. Within these classifications, the common groups of chemical sensors are electrical and electrochemical transducers, electrochemical, potentiometric, conductometric, amperometric, elastomer and chemiresistor sensor. Sometimes the chemical sensor is also grouped as part of biochemical sensor (biosensor, enzyme sensor, multi array sensor), electronic nose and tongues (Fraden 2010; Ho et al 2001). For example, a biosensor consists of sensitive biological material/molecule (enzyme, microorganism, tissue, etc), transducer (work as electrochemical, optical, etc.) and associated electronic or signal processor functions to display the result. Hulanicki et al (1991) classified chemical sensor based on operating principle of the transducer. Those are (1) optical sensor (measurement of absorbance, reflectance, luminescence, fluorescence, refractive index, optothermal effect, light scattering); (2) electrochemical device (volumetric, potentiometric sensors, chemically sensitized field effect transistor, potentiometric solid electrolyte gas sensor); (3) electrical device (metal oxide, organic semiconductor, electrolyte conductivity, electric permittivity sensors); (4) mass sensitive device (piezoelectric, surface acoustic wave, (5) magnetic device; (6) thermometric device and (7) other physical properties.

Chitosan based sensor

General uses. Since chitosan has both hydroxyl ($-\text{CH}_2\text{OH}$) and amino groups that provides lone pair electrons for metal ions, whereas $-\text{CH}_2\text{OH}$ might be oxidized to $-\text{CHO}$ or $-\text{COOH}$, chitosan functioned as both the protecting and the reducing agent in preparation of metal nanoparticles (Adlim & Bakar 2013; 2008a; 2008b; Adlim 2006; Adlim et al 2004). Since chitosan has affinity toward metal ions and the polymer has compatibility in aqueous system, chitosan has been widely used in sensor preparations.

Ye et al (1998) published studies on glassy electrode with slurry alumina coated with chitosan solution to prepare an electrochemical sensor for detection Au, Ag, Pt and Pd. The deviation detection from real concentration was 4.7% (Pt), 2.0% (Au), 1.6% (Ag) and 1.2% (Pd). Other chitosan based electrochemical sensor was for dimethyl disulfide detection that was reported by Rajabsadeh et al (2014). Sensor for Pb(II) was fabricated by Kucukkolbasi et al (2013) by using Schiff-base of chitosan-2,4 dihydroxy benzaldehyde as the active agent. Chitosan was also used as media to hold pyrene and β -cyclodextrin as the active reagent for sensing nitromethane (Wang et al 2003). Hydrogen peroxide sensor was assembly using horseradish peroxidase enzyme immobilized to gold nanoparticle modified chitosan-entrapped carbon paste electrode (Zhou et al 2002; Lei et al 2003). Similar chitosan function in sensor preparation for bisphenol A identification was reported by Huang et al (2014). Chitosan membrane containing 2-(4-pyridylazo)resorcinol was as a flow cell optosensor for Co(II) detection (Yusof & Ahmad 2002). Nickel (II) and antibiotic cefixime were immobilized in chitosan membrane and used for methanol sensor that worked with electro-oxidation process (Liu et al 2009).

Zhao et al (1998) employed chitosan as a medium to hold ruthenium complex on preparation of oxalic acid sensor. Similar function of chitosan was reported by Yao et al (2003). They used chitosan as a membrane support for uricase enzyme as the active agent for monitoring uric acid in vivo, a membrane for urea biosensor (Mulyasuryani et al 2010).

Mercury determination in water. Rhodamine derivative was grafted to chitosan surface has high affinity to Hg^{2+} ion. Binding Rhodamine to chitosan was confirmed based on data of the UV-vis spectra and Fourier transform-infrared spectroscopy. This matrix was not only as an absorbent for Hg^{2+} ion but also as excellent colorimetric and fluorescence turn-on “naked-eye” sensor. The sensor was also selective for mercury ions from among various metal ions. It gave linear response between fluorescence emission intensity and the concentration of Hg^{2+} in range of 0–6.0 μM with a detection limit of 3.42×10^{-6} M. The sensor probe was useable for several times of mercury adsorption (Shi et al 2015).

Abdi et al (2011) prepared thin layer gold on microscope glass slide by using sputtering coating technique. The second layer was electropolymerization deposition of a mixture; chitosan, pyrrole and p-toluene sulfonate. This working electrode was used to detect mercury and lead ions with Surface Plasmon Resonance (SPR) technique. Fluid cell containing sample of mercury or lead ions was attached to sensor probe as shown in Figure 3. There was linear correlation between SPR angle (resonance unit = RU) and the typical metal ion concentrations. Binding affinity of metal ions to chitosan-based sensor led to higher ΔRU . Sensor was more sensitive for Pb^{2+} rather than for Hg^{2+} because Pb^{2+} binds stronger to the polymer.

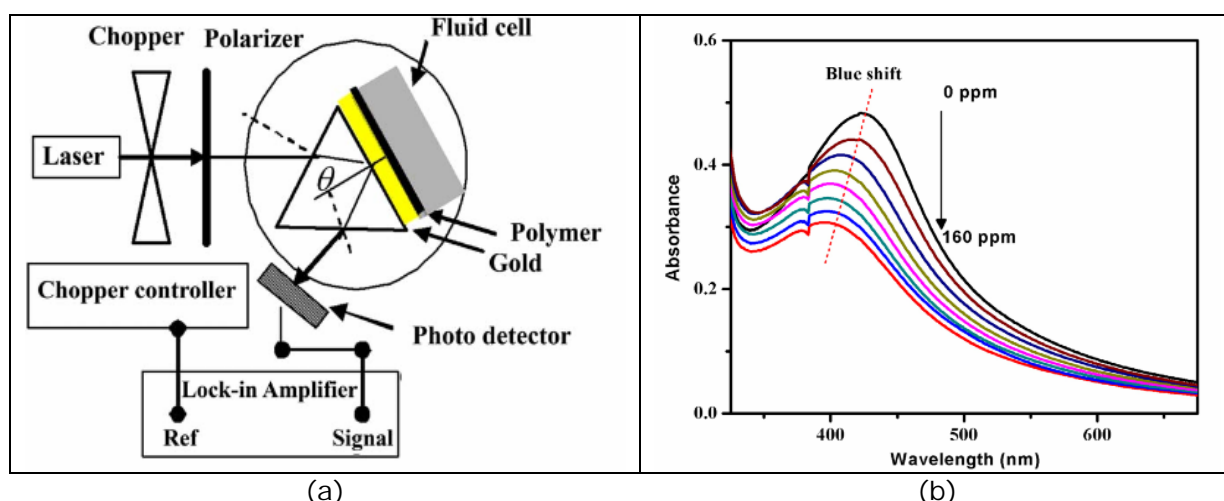


Figure 2. (a) Set up configuration for SPR equipment, Abdi et al (2011).
(b) UV-Vis spectra of AgNP showing response to mercury ions (Nivethaa et al 2015).

Chitosan was blended with graphite powder and inserted in cavity of pH-meter-electrode to prepare Chitosan Modified Carbon Paste Electrode (CMCPE) (Marcolino-Junior et al 2007). CMCPE was used as a working electrode for determination of mercury (II) ions by recording the anodic stripping voltamogram with a Potentiometer of a Potentiostat/Galvanostat Autolab PGSTAT (Ecochemie) controlled by GPES4.9 software. There was no significant difference at level of 95% confidence between mercury (II) concentrations measured by using official method and by this sensor as reported by Marcolino-Junior et al (2007).

Colorimetric sensor for mercury ion detection was reported by Chen et al (2015). The principal work of the sensor is the mercury ion led to aggregate gold metal nanoparticles. The aggregation change indicated by color intensity change from red to purple following the change of mercury concentration. In sensor preparation, gold nanoparticles (AuNP) was prepared by refluxed the gold ion within sodium citrate solution that acted as the reducing agent. This gold sol was suspended in various concentration of

chitosan solution and then, various concentration of mercury (II) ion was added. Each mixture was characterized by Transmission Electron Microscope (TEM) to measure the particle size and by UV-Vis spectrophotometer to record the color changes. Chen et al (2015) concluded that high concentration of chitosan led to low absorbance and less sensitivity of sensor. The optimum condition was 100 μL chitosan (0.1 mg mL^{-1}) was added into 900 μL AuNP solution. With UV-vis extinction peak at 524 nm, the color of the solution changed from wine-red to blue-purple gradually with an increase of the mercury concentration. Detection limit for Hg(II) was $1.35 \mu\text{M}$ below toxicity of mercury in drinking water ($30 \mu\text{M}$) defined by WHO (2005). Selectivity of the sensor for Hg^{2+} studied at $5 \mu\text{M}$ was obvious on color change (51.3%) compared to background, and there was very little change in presence of interference ions that is Fe^{3+} , Ba^{2+} , Cd^{2+} and Pb^{2+} . However significant color change (11.76-13.58%) was observed with Mg^{2+} , Ca^{2+} and Mn^{2+} interferences. Compared to ICP method, the accuracy of sensor at 0.25, 0.35, 0.375 M of Hg^{2+} in real sample was 98.1, 95.8, and 94.8% (Chen et al 2015).

Colloidal silver nanoparticles stabilized by chitosan were also used as a colorimetric sensor for mercury ion determination. A blue shift spectra and the intensity of UV-Vis spectra gradually decreased a long with increasing the mercury ion concentration. The detection limit was found as low as $7.2 \times 10^{-8} \text{ M}$ (Nivethaa et al 2015).

Liu et al (2015) reported that electrochemical biosensor for Hg^{2+} detection was fabricated from cupro-oxide and nano-chitosan composite. Cetyltrimethyl ammonium bromide and then Na_2SO_4 was added into chitosan solution subsequently to prepare nanocomposite chitosan residue (NCs). This residue was dissolved in acetic acid and cuprisulfate and glucose were added and the pH was adjusted at pH 10. This composite was immobilized on gold electrode. The electrode coated with composite was immersed in DNA before using a sensor for mercury detection. Liu et al (2015) reported the sensor has selectivity toward mercury among the interfering metal ions; Co^{2+} , Ag^+ , Ni^{2+} , Zn^{2+} , Fe^{3+} , and Pb^{2+} . The limit detection for Hg^{2+} was 0.15 nm L^{-1} .

Carbon nanotube assembled with crosslinked chitosan was used as an active agent in working electrode for detection of mercury (II) and cadmium(II) with Voltametric method. The anodic stripping voltammetry current was linear with Hg^{2+} concentration, in range from 6.7×10^{-9} to $8.3 \times 10^{-8} \text{ mol L}^{-1}$ with detection limit of $2.4 \times 10^{-9} \text{ mol L}^{-1}$ (Janegitz et al 2011).

Conclusions. Chitosan has been intensively studied in various applications including as material for sensor preparation to determine mercury in water. Mercury sensor was developed as a respond to the complexity of normal official procedure, while mercury pollution is already on the alert in environment. The portable mercury sensors were still under study and so far they might be effective in laboratory scale for determination of the total mercury concentration. The mercury species determination however, still remains as complicated procedure. The existence mercury species; mono- and dimethyl mercury in food chain is already reported although the transformation among mercury species in nature is still hypothetic based on analogical conclusion from laboratory condition.

References

- Abernathy A. R., Cumbie P. M., 1977 Mercury accumulation by largemouth bass (*Micropterus salmoides*) in recently impounded reservoirs. Bulletin of Environmental Contamination and Toxicology 17:595-602.
- Abdi M. M., Abdullah L. C., Sadrolhosseini A. R., Mat Yunus W. M., Moxsin M. M., Tahir P. M., 2011 Surface plasmon resonance sensing detection of mercury and lead ions based on conducting polymer composite. PLoS One 6(9):e24578.
- Adlim A., 2006 Immobilizing chitosan-stabilized palladium nanoclusters on titanium dioxide and their hydrogenation properties. Jurnal Matematika dan Sains 11:125-133.
- Adlim M., Bakar M. A., 2008a Preparation of chitosan-gold nanoparticles: Part 1. Effect of reducing technique. Indonesian Journal of Chemistry 8:184-188.

- Adlim M., Bakar M. A., 2008b Preparation of chitosan-gold nanoparticles: Part 2. The role of chitosan. *Indonesian Journal of Chemistry* 8:320-326.
- Adlim M., Bakar M. A., 2013 The properties of Pd/Au bimetallic colloidal catalysts stabilized by chitosan and prepared by simultaneous and stepwise chemical reduction of the precursor ions. *Kinetics and Catalysis* 54(5):586-596.
- Adlim M., Bakar M. A., Liew K. Y., Ismail J., 2004 Synthesis of chitosan-stabilized platinum and palladium nanoparticles and their hydrogenation activity. *Journal of Molecular Catalysis A: Chemical* 212:141–149.
- Amyot M., Morel F. M. M., Ariya P. A., 2005 Dark oxidation of dissolved and liquid elemental mercury in aquatic environments. *Environmental Science and Technology* 39:110-114.
- Azimi S., Sadeghi Moghaddam M., 2013 Effect of mercury pollution on the urban environment and human health. *Environment and Ecology Research* 1(1):12-20.
- Bansal N., Vaughan J., Boulemant A., Leong T., 2014 Determination of total mercury in bauxite and bauxite residue by flow injection cold vapour atomic absorption spectrometry. *Microchemical Journal* 113:36-41.
- Boscher A., Gobert S., Guignard C., Ziebel J., L'Hoste L., Gutleb A. C., Cauchie H. M., Hoffmann L., Schmidt G., 2010 Chemical contaminants in fish species from rivers in the North of Luxembourg: potential impact on the Eurasian otter (*Lutra lutra*). *Chemosphere* 78:785–792.
- Chen Z., Zhang C., Tan Y., Zhou T., Ma M., Wan C., Lin Y., Li K., 2015 Chitosan-functionalized gold nanoparticles for colorimetric detection of mercury ions based on chelation-induced aggregation. *Microchimica Acta* 182:611–616.
- Clever H. L., Johnson S. A., Derrick M. E., 1985 The solubility of mercury and some sparingly soluble mercury salts in water and aqueous electrolyte solutions. *Journal of Physical and Chemistry Reference Data* 14:631-680.
- Craig P. J., Jenkins R. O., 2004 Organometallic compounds in the environment: an overview. In: *Organic metal and metalloid species in the environment*. Himer A., Emon H. (eds), Berlin: Springer Berlin Heidelberg, pp. 1-15.
- D'Agostino F., Oliveri E., Bagnato E., Falco F., Mazzola S., Sprovieri M., 2014 Direct determination of total mercury in phosphate rock using alkaline fusion digestion. *Analytica Chimica Acta* 852:8-12.
- Da Silva M. J., Paim A. P. S., Pimentel M. H., Cervera M. L., de la Guardia M., 2014 Determination of total mercury in nuts at ultratrace level. *Analytica Chimica Acta* 838:13-19.
- DiFrancesco D. T., Shinn R. C. Jr., 2002 New Jersey mercury task force report 2002, Volume II, Exposure and Impact, pp. 55-68.
- Dhillon G. S., Kaur S., Brar S. K., Verma M., 2013 Green synthesis approach: extraction of chitosan from fungus mycelia. *Critical Reviews in Biotechnology* 33(4):379-403.
- Du M., Wei D., Tan Z., Lin A., Du Y., 2015 Predicted no-effect concentrations for mercury species and ecological risk assessment for mercury pollution in aquatic environment. *Journal of Environmental Sciences* 28:74-80.
- Ernawati Y., 2014 The analysis of the concentration of heavy metals cadmium, mercury and lead in the flesh of suckermouth catfish (*Pterygoplichthys pardalis*) in Ciliwung River, Indonesia. *AACL Bioflux* 7(1):33-42.
- FAO/WHO, 2003 Joint FAO/WHO expert committee on food additives, pp. 2-22. Available at: <http://ftp.fao.org/es/esn/jecfa/jecfa61sc.pdf>. Accessed: July 26, 2015.
- Fraden J., 2010 *Handbook of modern sensor: physic, design and application*. Fourth edition, New York, Springer, pp. 569-653.
- Ho C. K., Hughes R. C., Jenkins M. W., Lucero D. A., Itamura M. T., Kelley M., Reynolds P., 2001 Microchemical sensors for in-situ monitoring and characterization of volatile contaminants. In: *Proceedings of the 2001 International Containment and Remediation Technology Conference and Exhibition*, Orlando, Florida, June 10-13.
- Houserova P., Kuban V., Spurny P., Habarta P., 2006 Determination of total mercury and mercury species in fish and aquatic ecosystems of Moravian rivers. *Veterinarni Medicina* 51:101–110.

- Huang K. J., Liu Y. J., Liu Y. M., Wang L. L., 2014 Molybdenum disulfide nanoflower-chitosan-Au nanoparticles composites based electrochemical sensing platform for bisphenol A determination. *Journal of Hazardous Materials* 276:207–215.
- Hudson R. J. M., Gherini S. A., Watras C. J., Porcella D. B., 1994 Modeling the biochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes. In: *Mercury pollution: integration and synthesis*. Watras C. J. (ed), Lewis Publishers, Boca Raton, FL, pp. 473–523.
- Hulanicki A., Glab S., Ingman F., 1991 Chemical sensor definition and classification. *Pure and Applied Chemistry* 63(9):1247–1250.
- Janegitz B. C., Figueiredo-Filho L. C. S., Marcolino-Junior L. H., Souza S. P. N., Pereira-Filho E. R., Fatibello-Filho O., 2011 Development of a carbon nanotubes paste electrode modified with crosslinked chitosan for cadmium(II) and mercury(II) determination. *Journal of Electroanalytical Chemistry* 660:209–216.
- Kotnik J., Horvat M., Tessier E., Ogrinc N., Monperrus M., Amouroux D., Fajon V., Gibicar D., Zizek S., Sprovieri F., Pirrone N., 2007 Mercury speciation in surface and deep waters of the Mediterranean Sea. *Marine Chemistry* 107(1):13–30.
- Kucukkolbasi S., Erdogan Z. O., Berek J., Sahin M., Kocak N., 2013 A novel chitosan nanoparticle-schiff base modified carbon paste electrode as a sensor for the determination of Pb(II) in waste water. *International Journal of Electrochemical Science* 8:2164–2181.
- Lei C. X., Hu S. Q., Shen G. L., Yu, R. Q., 2003 Immobilization of horseradish peroxidase to a nano-Au monolayer modified chitosan-entrapped carbon paste electrode for the detection of hydrogen peroxide. *Talanta* 59:981–988.
- Leopold K., Foulkes M., Worsfold P., 2010 Methods for the determination and speciation of mercury in natural waters - a review. *Analytica Chimica Acta* 663:127–138.
- Li Z., Xia S., Wang J., Bian C., Tong J., 2015 Determination of trace mercury in water based on N-octylpyridinium ionic liquids preconcentration and stripping voltammetry. *Journal of Hazardous Materials* 301:206–213.
- Liu S., Kang M., Yan F., Peng D., Yang Y., He L., Wang M., Fang S., Zhang Z., 2015 Electrochemical DNA biosensor based on microspheres of cuprous oxide and nano-chitosan for Hg(II) detection. *Electrochimica Acta* 160:64–73.
- Liu Y., Luo S., Wei W., Liu X., Zeng X., 2009 Methanol sensor based on the combined electrocatalytic oxidative effect of chitosan-immobilized nickel(II) and antibiotic cefixime on the oxidation of methanol in alkaline medium. *Microchimica Acta* 164:351–355.
- Magalhães M. E., Tubino M., 1995 A possible path for mercury in biological systems: the oxidation of metallic mercury by molecular oxygen in aqueous solutions. *Science of the Total Environment* 170:229–239.
- Mandjukov P., Orani A. M., Han E., Vassileva E., 2015 Determination of total mercury for marine environmental monitoring studies by solid sampling continuum source high resolution atomic absorption spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* 103–104:24–33.
- Maršálek P., Svobodová Z., 2006 Rapid determination of methylmercury in fish tissues. *Czech Journal of Food Science* 24(3):138–142.
- Marcolino-Junior L. H., Janegitz B. C., Lourencao B. C., Fatibello-Filho O., 2007 Anodic stripping voltammetric determination of mercury in water using chitosan-modified carbon paste electrode. *Analytical Letters* 40:3119–3128.
- Mason R. P., Fitzgerald W. F., 1991 Mercury speciation in open ocean waters. *Water, Air and Soil Pollution* 56:779–789.
- Mulyasuryani A., Roosdiana A., Srihardyastutie A., 2010 The potentiometric urea biosensor using chitosan membrane. *Indonesian Journal of Chemistry* 10(2):162–166.
- Niazi A., Habibi S., Ramezani M., 2015 Preconcentration and simultaneous spectrophotometric determination of copper and mercury by dispersive liquid–liquid microextraction and orthogonal signal correction–partial least squares. *Arabian Journal of Chemistry* 8(5):706–714.

- Nivethaa E. A., Narayanan V., Stephen A., 2015 Synthesis and spectral characterization of silver embedded chitosan matrix nanocomposite for the selective colorimetric sensing of toxic mercury. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 143:242-250.
- NRDC, 2000 Mercury contamination in fish. Available at: <http://www.nrdc.org/health/effects/mercury/sources.asp>. Accessed: July 25, 2015.
- Panichev N. A., Panicheva S. E., 2015 Determination of total mercury in fish and sea products by direct thermal decomposition atomic absorption spectrometry. *Food Chemistry* 166:432-441.
- Paul S., Jayan A., Sasikumar C. S., Cherian S. M., 2014 Extraction and purification of chitosan from chitin isolated from sea prawn (*Fenneropenaeus indicus*). *Asian Journal of Pharmaceutical Clinic Research* 7(4):201-204.
- Prokopowicz A., Mniszek W., 2005 Mercury vapor determination in hospitals. *Environmental Monitoring and Assessment* 104:147-154.
- Qazi H. H., Mohammad A. B., Akram M., 2012 Review on recent progress in optical chemical sensors. *Sensors* 12:16522-16556.
- Rajabzadeh S., Rounaghi G. H., Arbab-Zavar M. H., Ashraf N., 2014 Development of a dimethyl disulfide electrochemical sensor based on electrodeposited reduced graphene oxide-chitosan modified glassy carbon electrode. *Electrochimica Acta* 135:543-549.
- Rinaudo M., 2006 Chitin and chitosan: properties and applications. *Progress in Polymer Science* 31:603-632.
- Rodgers D. W., 1982 Dynamics of methylmercury accumulation in rainbow trout (*Salmo gairdneri*). PhD Thesis, University of Guelph, Guelph, 129 pp.
- Schaefer J. K., Morel F. M. M., 2009 High methylation rates of mercury bound to cysteine by *Geobacter sulfurreducens*. *Natural Geoscience* 2:123-126.
- Schaefer J. K., Rocks S. S., Zheng W., Liang L., Gu B., Morel F. M., 2011 Active transport, substrate specificity, and methylation of Hg(II) in anaerobic bacteria. *Proceedings of the National Academy of Sciences of the USA* 108(21):8714-8719.
- Scheuhammer A., Braune B., Chan H. M., Frouin H., Krey A., Letcher R., Loseto L., Noël M., Ostertag S., Ross P., Wayland M., 2015 Recent progress on our understanding of the biological effects of mercury in fish and wildlife in the Canadian Arctic. *Science of the Total Environment* 509-510:91-103.
- Sekhar P. K., Brosha E. L., Mukundan R., Garzon F. H., 2010 Chemical sensors for environmental monitoring and homeland security. *The Electrochemical Society Interface*, pp. 35-40.
- Shukla S. K., Mishra A. K., Arotiba O. A., Mamba B. B., 2013 Chitosan-based nanomaterials: a state-of-the-art review. *International Journal of Biological Macromolecules* 59:46-58.
- Shi D., Yan F., Wang M., Zou Y., Zheng T., Zhou X., Chen L., 2015 Rhodamine derivative functionalized chitosan as efficient sensor and adsorbent for mercury(II) detection and removal. *Materials* 70:958-964.
- Stetter J. R., Penrose W. R., Yao S., 2003 Sensors, chemical sensors, electrochemical sensors, and ECS. *Journal of the Electrochemical Society* 150(2):11-16.
- Stokes P. M., Wren C. D., 1987 Bioaccumulation of mercury by aquatic biota in hydroelectric reservoirs: a review and consideration of mechanisms. In: Lead, mercury, cadmium and arsenic in the environment. Hutchinson T. C., Meema K. M. (eds), John Wiley & Sons Ltd., pp. 255-277.
- Van Straaten P., 2000 Mercury contamination associated with small-scale gold mining in Tanzania and Zimbabwe. *The Science of the Total Environment* 259:105-113.
- Wang H., Fang Y., Ding L., Gao L., Hu D., 2003 Preparation and nitromethane sensing properties of chitosan thin films containing pyrene and b-cyclodextrin units. *Thin Solid Films* 440:255-260.
- World Health Organization (WHO), 2005 Mercury in drinking water. WHO/SDE/WSH/05.08/10. Available at: www.who.int/water_sanitation.../mercuryfinal.pdf. Accessed: Sept 26, 2015.

- Wood J. M., Kennedy F. S., Rosen C. G., 1968 Synthesis of methyl-mercury compounds by extracts of a methanogenic bacterium. *Nature* 220(5163):173–174.
- Yamamoto M., 1995 Possible mechanism of elemental mercury oxidation in the presence of SH compounds in aqueous solution. *Chemosphere* 31:2791-2798.
- Yamamoto M., 1996 Simulation of elemental mercury oxidation in the presence of chloride ion in aquatic environments. *Chemosphere* 32:1217-1224.
- Yao D., Vlessidis A. G., Evmiridis N. P., 2003 Microdialysis sampling and monitoring of uric acid in vivo by a chemiluminescence reaction and an enzyme on immobilized chitosan support membrane. *Analytica Chimica Acta* 478:23–30.
- Ye X., Yang Q., Wang Y., Li N., 1998 Electrochemical behavior of gold, silver, platinum and palladium on the glassy carbon electrode modified by chitosan and its application. *Talanta* 47:1099-1106.
- Yuan C. G., Li Q. P., Feng Y. N., Chang A. L., 2010 Fraction and leaching characteristics of mercury in coal. *Environmental Monitoring and Assessment* 167:581-586.
- Yusof N. A., Ahmad M., 2002 A flow cell optosensor for determination of Co(II) based on immobilized 2-(4-pyridylazo)resorcinol in chitosan membrane by using stopped flow, flow injection analysis. *Sensor and Actuator B* 86:127-133.
- Zhao C. Z., Egashira N., Kurauchi Y., Ohga K., 1998 Electrochemiluminescence oxalic-acid sensor having a platinum-electrode coated with chitosan modified with a ruthenium (II) complex. *Electrochimica Acta* 43(14-15):2167-2173.
- Zhou G. J., Wang G., Xu J. J., Chen, H. Y., 2002 Reagentless chemiluminescence biosensor for determination of hydrogen peroxide based on the immobilization of horseradish peroxidase on biocompatible chitosan membrane. *Sensor and Actuator B* 81:334-339.
- *** <http://dalwoo.tripod.com/structure.gif>.
- *** www.nrdc.org.

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