UNIVERSITI PUTRA MALAYSIA

MOLECULARLY IMPRINTED POLYMER FOR THE REMOVAL OF MERCURY FROM PETROLEUM OIL

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MOLECULARLY IMPRINTED POLYMER FOR THE REMOVAL OF MERCURY FROM PETROLEUM OIL

By

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Thesis Submitted to the School of Graduate Studies,Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

MOLECULARLY IMPRINTED POLYMER FOR THE REMOVAL OF MERCURY FROM PETROLEUM OIL

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Chairman : Nor Azah Yusof, PhD
Faculty : Science

Mercury (Hg) is a contaminant is many natural products including hydrocarbon fuels. The presence of mercury can cause problems with downstream processing units as well as safety of workers and environmental issues. Such concern provides incentive to remove the mercury from petroleum oil. Therefore, improvise sorbents is still essential to be further investigates. In recent years, molecularly imprinted polymers (MIPs) have attracted the attention of several researches due to their capability for molecular recognition, easiness of preparation, stability and cost-effective production. By taking advantage of these facts, Hg(II) imprinted polymer and non-imprinted polymer (NIP) were synthesized by bulk polymerization method where cysteine complex (or L-cysteine alone) was polymerized with mercury nitrate (or without it) as a template. Then, methacrylic acid (MAA), 2-hydroxylethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) and methanol were added as monomer, co-monomer, cross-linker and solvent respectively. The obtained MIPs were crushed and sieved. The total weight of yield of MIP increased with increasing ratio of monomer, cysteine complex and cross-linker. The temperature used during polymerization was standardized to 70.0°C. The best ratio of monomer to cross-linker is 1:5 while the amount of cysteine complex is 2.0 mmol.

FTIR results displayed the presence of S-H in the cysteine complex but there is no peak of S-H observed in MIP-CC spectrum which conclude the interaction between S-H and Hg(II) has occurred. FESEM shows that MIP possess spherical and densely packed particles with rough surface compared with NIP for both cysteine complex (CC) and L-cysteine(LC). Through BET result, the surface area and pore volume of MIP-CC is larger than NIP-CC while for MIP-LC and NIP-LC is vice versa. From TGA result, monomer MAA fully decomposed at lower temperature (197.0°C) compared with MIP-CC, NIP-CC, MIP-LC and NIP-LC.

The optimum sorption capacity during pH studies was achieved at pH 7 for both MIP-CC and MIP-LC. Besides, the sorption of Hg(II) increased by increasing the dosage of MIP. Both MIP-CC and MIP-LC followed Freundlich isotherm with R^2=0.9551 and R^2 =0.9505 respectively. Meanwhile, the sorption of Hg(II) by MIP is fast within a few second and it is well fitted with pseudo second order reaction. The selectivity result shows that MIP-CC exhibit high selectivity and affinity towards Hg(II) in the presence of competitor ions; Pb(II), Zn(II) and Cd(II) compared with MIP-LC. The reusability of the MIP-CC particles was tested for four times and no significant loss in sorption capacity was observed. From the real samples analysis, the sorption capacities obtained were 93.8% for sludge sample and 29.8% for crude petroleum oil sample with initial Hg(II) concentration of 74.6 μg/L and 1.78μg/L respectively

A new type of Hg(II) imprinted polymer as a sorbents for removal of mercury from petroleum oil was successfully synthesized. Prepared MIP-CC showed several characteristic such as high thermal stability, fast sorption kinetic and proper selectivity of Hg(II). Thus, MIP-CC can be potentially used as a sorbents for the removal of mercury petroleum oil.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

POLIMER CETAKAN MOLEKUL UNTUK PENYINGKIRAN MERKURI DARIPADA MINYAK PETROLEUM

Oleh

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Merkuri (Hg) adalah bahan cemar di dalam banyak produk semulajadi termasuk minyak hidrokarbon. Kehadiran merkuri boleh menyebabkan banyak masalah dengan unit pemprosesan hiliran serta keselamatan perkerja dan isu-isu alam sekitar. Kebimbangan sedemikian menyediakan insentif untuk menyingkirkan merkuri daripada minyak petroleum. Oleh itu, menambah baik penjerap masih penting untuk kajian lanjut. Dalam beberapa tahun kebelakangan ini, polimer cetakan molekul (MIP) telah menarik perhatian oleh beberapa pengkaji disebabkan oleh keupayaan ia untuk mengenalpasti molekul, kemudahan semasa penyediaan, kestabilan dan kos pengeluaran yang efektif Dengan mengambil kesempatan daripada fakta-fakta ini, cetakan polimer Hg(II) dan polimer bukan cetakan molekul (NIP) telah disintesis melalui kaedah pempolimeran pukal dimana kompleks sistin (atau L-sistin sahaja) dipolimerkan bersama merkuri nitrat (atau tanpanya) sebagai acuan. Selepas itu, asid metakrilik (MAA), 2-hidrosietil metakrilat (HEMA), etilena gliko dimetilenakrilat (EGDMA) dan metanol ditambahkan sebagai monomer, monomer bersama, penggabung dan pelarut bagi setiap masing-masing. MIP yang diperolehi dengan itu dihancurkan dan ditapis. Jumlah berat hasil MIP bertambah dengan peningkatan nisbah monomer, sistin-kompleks dan penggabung. Suhu yang digunakan semasa polimeran diselaraskan pada suhu 70.0°C. Nisbah yang terbaik bagi monomer dan penggabung ialah 1:5 manakala jumlah sistin kompleks ialah 2.0 mmol.

Hasil FTIR yang diperolehi menunjukkan kehadiran S-H dalam spektrum sistin kompleks tetapi tidak ada puncak S-H diperhatikan dalam spektrum MIP-CC. Kesimpulannya, interaksi antara S-H dan Hg(II) telah berlaku. FESEM menunjukkan bahawa MIP mempunyai zarah sfera dan padat dengan permukaan kasar berbanding dengan NIP bagi kedua-dua sistin kompleks (CC) dan L-sistin (LC). Melalui hasil BET, jumlah luas permukaan dan isipadu liang MIP-CC lebih besar berbanding NIP-CC sementara bagi MIP-LC dan NIP-LC adalah sebaliknya. Daripada hasil TGA, monomer MAA terurai sepenuhnya pada suhu yang rendah (197.0°C) berbanding dengan MIP-CC, NIP-CC, MIP-LC dan NIP-LC.

Kapasiti penjerapan optimum semasa ujian pH telah dicapai pada pH 7 bagi kedua-dua MIP-CC dan MIP-LC. Selain itu, penjerapan Hg(II) meningkat dengan peningkatan dos MIP. Kedua-dua MIP-CC dan MIP-LC mengikut isoterma Freundlich dengan R^2 = 0.9551 dan R^2 = 0.9505 bagi setiap masing-masing. Sementara itu, penjerapan Hg(II) oleh MIP adalah pantas dalam masa beberapa saat dan ianya sesuai dengan tindak balas tertib kedua. Hasil selektiviti menunjukkan bahawa MIP-CC mempunyai selektiviti yang tinggi dan tertarik kepada Hg(II) dengan kehadiran ion pesaing ; Pb(II), Zn(II) dan Cd(II) berbanding dengan MIP-LC. Kebolehgunaan semula zarah MIP-CC telah diuji sebanyak empat kali dan tiada penurunan ketara pada kapasiti penjerapan yang diperhatikan. Daripada analisis sampel yang sebenar, kapasiti penjerapan diperolehi ialah 93.8% bagi sampel mendapan dan 29.8% bagi sampel minyak petroleum mentah dengan bacaan awal kepekatan Hg(II) adalah 74.6 μg/L dan 1.78μg/L masing-masing.

Hg(II) cetakan polimer yang baharu sebagai penjerap untuk penyingkiran merkuri daripada minyak petroleum telah berjaya disintesis. MIP-CC yang disedia menujukkan ciri-ciri seperti kestabilan haba yang tinggi, kinetic penjerapan pantas dan selektiviti terhadap Hg(II). Oleh itu, MIP-CC berpotensi digunakan sebagai penjerap untuk penyingkiran minyak daripada minyak petroleum.

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I certify that a Thesis Examination Committee has met on 8 August 2016 to conduct the final examination of Nor Ain Shahera binti Khairi on her thesis entitled "Molecularly Imprinted Polymer for Removal of Mercury from Petroleum Oil" 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 Master of Science.

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LIST OF ABBREVIATIONS

ATR	Attenuated Total Reflectance
BET	Brunauer Emmett Teller
CC	Cysteine-complex
DTG	Differential Thermogravimetric Analysis
EGDMA	Ethylene Glycol Dimethacrylate
FTIR	Fourier Transform Infrared
FESEM	Field Emission Scanning Electron Microscopy
HEMA	2-Hydoxylethyl Methacrylate
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LC	L-cysteine
MAA	Methacrylic Acid
MATAC	2-(Methacryloyloxy)ethyl] Trimethyl Ammonium Chloride
MIP	Molecularly Imprinted Polymer
NIP	Non-molecularly Imprinted Polymer
MIP-CC	Molecularly Imprinted Polymer- Cysteine-complex
NIP-CC	Non-molecularly Imprinted Polymer Cysteine-Complex
MIP-LC	Molecularly Imprinted Polymer-L-cysteine
NIP-LC	Non-molecularly Imprinted Polymer-L-Cysteine
SPE	Solid Phase Extraction
TGA	Thermal Gravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Mercury is one of the hazardous heavy metals both to human and ecosystem because it is highly toxic to central nervous system and tends to bio-accumulate in the human body. This will lead to a variety of adverse health effects including neurological, renal, respiratory, immune, dermatologic and reproductive and developmental neurotoxicity (Poulin, Prüss-üstün, & Gibb, 2008). Mercury exists in various forms which are elemental mercury, inorganic mercury and organic mercury. All these forms have different toxicities and implication for health. According to World Health Organization, WHO guideline values, the limitation of mercury inside water is 1μg/L for total mercury, 1μg/m^3 mercury in air. In addition, WHO estimated a tolerable concentration of 0.2 μg/m^3 for long-term inhalation exposure to elemental mercury vapor and a tolerable intake of total mercury of 2 μg/kg body weight per day (WHO, 2007).

The major sources of mercury emission are from natural, anthropogenic and re-emitted sources, whereas the most crucial anthropogenic sources are urban discharges, agriculture discharge, mining and combustion and industrial discharge. Combusted hydrocarbon fuels originates from petroleum and coal was also included as one of the major anthropogenic sources of mercury emissions to US according to US EPA 1997 (Diseases, 2008). Relatively, light hydrocarbon liquids which are crude oil, condensate, natural gas and the like produced from wells and exhaust combustion gas sometime contain mercury or mercury compound. Thus, this will contribute to several negative impacts on gas processing operation such as equipment degradation, toxic waste generation, increase risk to the health and safety of workers and poisoning of catalyst (Wilhelm & Bloom, 2000)

Mercury removal sorbent beds are used to scavenge the mercury from gas and liquid hydrocarbon streams. Several commercial processes are available for removing mercury and mercury compound from hydrocarbon but selection of the most effective system must be predicated since some of the mercury removal systems are targeted at gas phase treatment and some are targeted at liquids. Gas phase treatment systems primarily consist of sulfur impregnated carbon (U.S. Patent 8,598,072 B2), metal sulfide on carbon or alumina and regenerative molecular sieve. As for hydrocarbon liquid streams, the systems consist of iodide-impregnated carbon, metal sulfide on carbon or alumina, a mol sieve amalgam system and a two-step processing consisting of a hydrogenation conversion catalyst followed by metal sulfide reaction with elemental mercury. All the commercialized methods have both advantages and disadvantages that depend on feed composition and stream location.

In recent years, molecular imprinting has attracted considerable interest in many areas of chemistry, biochemistry and biotechnology owing to their high degree of selectivity and affinity towards the target molecule. Molecular imprinted polymers (MIPs)

applications including biosensor and chemosensor, microreactor, solid phase extraction (SPE), affinity chromatography and catalysis. The latest development in the technique of molecular imprinting have made an available polymers that can be used in the detection of drugs, toxins, pesticides, food components and other molecules that would be difficult to isolate otherwise.

MIPs were described as artificial synthesized macromolecular materials with prearrangement of structure and specific molecular recognition ability. This unique ability can recognize the template molecule used in the imprinting process even in the presence of compounds that having similar structure and functionality to the template. The MIPs tend to be simple and inexpensive to prepare and are generally rather robust in nature. MIPs also offer several advantages including the ability to tolerate high pressures, organic solvents, pH extremes and elevated temperature. Due to high degree cross-linking of MIPs, it provides distinctive chemical, mechanical and thermal long stability compared with their biological counterparts (Koesdjojo et al., 2007).

MIPs are generally prepared by involving the complexation in solution of a template molecule with functional monomers through covalent bonds followed by polymerization of these monomers around the template with the help of a cross-linker in the presence of an initiator. After the polymerization process, the template molecule are removed by extensive washing steps to disrupt the interactions between the template and the monomers thus leaving the cavities of binding sites that are complementary to the template in size, shape and position of the functional group (Pichon & Chapuis-Hugon, 2008). Hence, the obtained cavities can work as selective binding sites for the template molecule.

MIPs can be synthesized by three different imprinting approaches which are covalent, non-covalent and semi-covalent. Non-covalent approach become the most applied technique compared to the other approaches due to its generality and simplicity during the process of template removal and the resulting greater numbers of higher affinity sites. As for covalent route, it lack of general applicability due to difficulty in finding a suitable monomer to conjugate to the template. Non-covalent imprinting involving self-assembly of the template with functional monomer prior to polymerization, free radical polymerization with the cross-linking monomer and then template extraction followed by rebinding via non-covalent interaction such as hydrogen bonds, ion pairs, dipole-dipole interaction and Van der Walls forces (Caro et al., 2002).

1.2 Statement of Problem

The toxic effects of mercury have been observed for centuries. Mercury has been classified as one of the top ten hazardous heavy metals according to World Health Organization (WHO). This is because of its reactivity, extreme volatility and its relative solubility in water and living tissues. The detection of mercury has long held the intention of analytical community and as such, a large number of protocols have arisen. One of the major anthropogenic sources is from combusted hydrocarbon that originates from petroleum oil. The concentration of mercury in crude oil and natural gas is highly

dependent on geologic location and varies between approximately 0.01 ppb and 10 ppm. Although the total amount of mercury and mercury compound is considered low, but it give detrimental impacts on petroleum process. In addition, water streams that are by-products of equipment cleaning and water condensed from glycol regeneration can contain high concentrations of mercury that will cause aquatic contamination if severe treatment does not take place.

Various commercial methods are available in industries for mercury removal systems for hydrocarbon streams such as sulfur-impregnated carbon, metal sulfide on carbon or alumina, zeolite, activated carbon and so on. However, there are several disadvantages of this commercialized method for examples mol-sieve amalgamation sorbents do not operate at high efficiencies if organic forms of mercury are present in significant concentration. Other than that, sulfur-impregnated carbons are soluble in liquid hydrocarbon and cannot be used in process locations. For these reason, the sorbents that have ability to tolerate high pressures, organic solvents and provide high chemical and mechanical stability is still essential to be further investigates.

The aim of this research is to prepare molecular imprinted polymer (MIP) which can be used for the selective removal of mercury in mercury removal system. In this research, the method of initiation use will be free radical or chain growth polymerization. It is the most important method available today for the conversion of monomer into polymer and is exploited widely in industries. The parameter studies including pH studies, dosage studies, sorption kinetics, sorption isotherms, selectivity and reusability studies. Considering the versatility and high level selectivity and recognition that can be achieved, the future use of MIPs as a sorbents in mercury removal system is very promising.

1.3 Objectives:

The objectives of this study are:

1. To synthesize molecularly imprinted polymer (MIP) for the removal of mercury(II) ions.
2. To distinguish the MIP and NIP by spectroscopy analysis, morphological characterization, thermal studies and surface area and porosity analysis.
3. To study the binding capacity of mercury(II) ions toward MIP based on pH, kinetic, isotherm, selectivity and reusability.
4. To investigate the removal of mercury(II) ions from actual samples; crude oil and condensate.

REFERENCES

Abbasi, S., Roushani, M., Khani, H., Sahraei, R., & Mansouri, G. (2015). Synthesis and application of ion-imprinted polymer nanoparticles for the determination of nickel ions. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, 140: 534–43.

Ahmed, M. J., & Dhedan, S. K. (2012). Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons. *Fluid Phase Equilibria*, 317: 9–14.

Andaç, M., Mirel, S., Senel, S., Say, R., Ersöz, A., & Denizli, A. (2007). Ion-imprinted beads for molecular recognition based mercury removal from human serum. *International Journal of Biological Macromolecules*, 40(2): 159–66.

Ayg, C. P. H., & Blankenship, D. W. (1984). The removal of mercury (ii) from dilute aqueous solution by activated carbon, (l): 37–46.

Bayramoglu, G., & Arica, M. Y. (2011). Synthesis of Cr(VI)-imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) particles: its adsorption propensity to Cr(VI). *Journal of Hazardous Materials*, 187(1-3): 213–21.

Bektas, S., & Denizli, A. (2002). Cysteine-metal affinity chromatography : determination of heavy metal adsorption properties, 26: 273–281.

Beltran, a, Marcé, R. M., Cormack, P. a G., & Borrull, F. (2010). Synthetic approaches to parabens molecularly imprinted polymers and their applications to the solid-phase extraction of river water samples. *Analytica Chimica Acta*, *677*(1), 72–8.

Braden et al., Removal of mercury and mercuric compounds from crude oil streams, U.S.Patent 8,524,074 B2; (Sept 2013)

Branger, C., Meouche, W., & Margaillan, A. (2013). Recent advances on ion-imprinted polymers. *Reactive and Functional Polymers*, 73(6): 859–875.

Caro, E., Masqué, N., Marcé, R. M., Borrull, F., Cormack, P. a G., & Sherrington, D. C. (2002). Non-covalent and semi-covalent molecularly imprinted polymers for selective on-line solid-phase extraction of 4-nitrophenol from water samples. *Journal of Chromatography. A*, 963(1-2): 169–78.

Chang, X., Jiang, N., Zheng, H., He, Q., Hu, Z., Zhai, Y., & Cui, Y. (2007). Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique. *Talanta*, 71(1): 38–43.

Chojnacki, a., Chojnacka, K., Hoffmann, J., & Górecki, H. (2004). The application of natural zeolites for mercury removal: from laboratory tests to industrial scale. *Minerals Engineering*, 17(7-8): 933–937.

Cormack, P. a G., & Elorza, A. Z. (2004). Molecularly imprinted polymers: synthesis and characterisation. *Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences*, 804(1): 173–82.

Daniel, S., Prabhakara Rao, P., & Prasada Rao, T. (2005). Investigation of different polymerization methods on the analytical performance of palladium(II) ion imprinted polymer materials. *Analytica Chimica Acta*, 536(1-2): 197–206.

Dekhil, A.B.; Hannachi, Y.; Ghorbel, A.; Baubaker, T. (2011) Comparative study of the removal of cadmium from aqueos solution by low cost adsorbents. *J. Environ. Sci. Technol*. 4: 520–533

Diseases, F. (2008). Issued by UNEP DTIE Chemicals Branch and, (August).

Dou, B., & Chen, H. (2011). Removal of toxic mercury(II) from aquatic solutions by synthesized TiO2 nanoparticles. *Desalination*, 269(1-3): 260–265.

Esen, C., Andac, M., Bereli, N., Say, R., Henden, E., & Denizli, A. (2009). Highly selective ion-imprinted particles for solid-phase extraction of Pb2+ ions. *Materials Science and Engineering: C*, 29(8): 2464–2470.

Exposure of mercury: A major public health concern, public health and environment, World Health Organization (WHO), 2007. Geneva, Switzerland.

Fan, J.-P., Tian, Z.Y., Tong, S., Zhang, X.H., Xie, Y.L., Xu, R., Ouyang, X.K. (2013). A novel molecularly imprinted polymer of the specific ionic liquid monomer for selective separation of synephrine from methanol-water media. *Food Chemistry*, 141(4): 3578–85.

Fan, Z. (2006). Hg(II)-imprinted thiol-functionalized mesoporous sorbent micro-column preconcentration of trace mercury and determination by inductively coupled plasma optical emission spectrometry. *Talanta*, 70(5): 1164–9.

García-Calzón, J. a., & Díaz-García, M. E. (2007). Characterization of binding sites in molecularly imprinted polymers. *Sensors and Actuators B: Chemical*, 123(2): 1180–1194.

Hall, A. J., Lanza-Sellergren, F., Manesiotis, P., & Sellergren, B. (2005). Non-covalent imprinting of phosphorous esters. *Analytica Chimica Acta*, 538(1-2): 9–14.

Hamad et al., Method for removing mercury form a gaseous or liquid stream, US Patent 8,641,890 B2, (Feb 2014).

Hashim, S. N. N. S., Boysen, R. I., Schwarz, L. J., Danylec, B., & Hearn, M. T. W. (2014). A comparison of covalent and non-covalent imprinting strategies for the synthesis of stigmasterol imprinted polymers. *Journal of Chromatography. A*, *1359*, 35–43.

He, C., Long, Y., Pan, J., Li, K., & Liu, F. (2007). Application of molecularly imprinted polymers to solid-phase extraction of analytes from real samples. *Journal of Biochemical and Biophysical Methods*, 70(2): 133–50.

Ho, Y. S., & Mckay, G. (1999). Pseudo-second order model for sorption processes, *Process Biochemistry*, 34: 451–465.

Ho, Y.-S., & Ofomaja, A. E. (2006). Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber. *Journal of Hazardous Materials*, 129(1-3): 137–42.

Ismaiel, A. A., Aroua, M. K., & Yusoff, R. (2013). Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the removal of mercury from contaminated water. *Chemical Engineering Journal*, 225: 306–314.

Jiang, X., Jiang, N., Zhang, H., & Liu, M. (2007). Small organic molecular imprinted materials: their preparation and application. *Analytical and Bioanalytical Chemistry*, 389(2): 355–68.

Kamra, T., Chaudhary, S., Xu, C., Montelius, L., Schnadt, J., & Ye, L. (2016). Journal of Colloid and Interface Science Covalent immobilization of molecularly imprinted polymer nanoparticles on a gold surface using carbodiimide coupling for chemical sensing, *461*, 1–8.

Khajeh, M., Yamini, Y., Ghasemi, E., Fasihi, J., & Shamsipur, M. (2007). Imprinted polymer particles for selenium uptake: synthesis, characterization and analytical applications. *Analytica Chimica Acta*, 581(2): 208–13.

Koesdjojo, M.T., Tennico, Y.H., Remcho, V.T. (2007). Molecularly imprinted polymers as sorbents for separation and extractions. In S*eparation Science and Technology:HPLC Method Development for pharmacutical;* Ahuja S., Rasmussen, H., Eds.; Academic Press : New Jersey, NJ, USA, 2007; Volume 8, pp, 479-503

Laatikainen, K., Udomsap, D., Siren, H., Brisset, H., Sainio, T., & Branger, C. (2015). Effect of template ion-ligand complex stoichiometry on selectivity of ion-imprinted polymers. *Talanta*, 134C: 538–545.

Li, Y., Fu, Q., Liu, M., Jiao, Y.-Y., Du, W., Yu, C., … Lu, J. (2012). Separation and enrichment of trace ractopamine in biological samples by uniformly-sized molecularly imprinted polymers. *Journal of Pharmaceutical Analysis*, 2(6): 395–402.

Liu, Y., Chang, X., Wang, S., Guo, Y., Din, B., & Meng, S. (2004). Solid-phase extraction and preconcentration of cadmium(II) in aqueous solution with Cd(II)-imprinted resin (poly-Cd(II)-DAAB-VP) packed columns. *Analytica Chimica Acta*, 519(2): 173–179.

Liu, Y., Chang, X., Yang, D., Guo, Y., & Meng, S. (2005). Highly selective determination of inorganic mercury(II) after preconcentration with Hg(II)-imprinted diazoaminobenzene–vinylpyridine copolymers. *Analytica Chimica Acta*, 538(1-2): 85–91.

Luliński, P., & Maciejewska, D. (2013). Effect of functional monomers and porogens on morphology, structure and recognition properties of 2-(4-methoxyphenyl)ethylamine imprinted polymers. *Materials Science & Engineering. C, Materials for Biological Applications*, 33(3): 1162–9.

Martín-Esteban, a. (2013). Molecularly-imprinted polymers as a versatile, highly selective tool in sample preparation. *TrAC Trends in Analytical Chemistry*, 45(1): 169–181.

Matvita et al., Mercury adsorbent carbon molecular sieves and process for removing mercury vapor from gas streams, U.S. Patent 4,708,853; (Nov 1987)

Mayes, a G., & Whitcombe, M. J. (2005). Synthetic strategies for the generation of molecularly imprinted organic polymers. *Advanced Drug Delivery Reviews*, 57(12): 1742–78.

Mijangos, I., Navarro-Villoslada, F., Guerreiro, A., Piletska, E., Chianella, I., Karim, K., Piletsky, S. (2006). Influence of initiator and different polymerisation conditions on performance of molecularly imprinted polymers. *Biosensors & Bioelectronics*, 22(3): 381–7.

Mohamad Yusof, N. N., Tanioka, E., & Kobayashi, T. (2014). Molecularly imprinted polymer particles having coordinated hydrogen bonding in covalent-imprinting for efficient recognition towards vanillin. *Separation and Purification Technology*, *122*, 341–349.

Nasirimoghaddam, S., Zeinali, S., & Sabbaghi, S. (2015). Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples. *Journal of Industrial and Engineering Chemistry*, 27: 79–87.

Novikova, G. V, Petrov, A. I., Staloverova, N. A., Shubin, A. A., & Dergachev, I. D. (2014). Complex formation of Sn (II) with L -cysteine : An IR , DTA / TGA and DFT Investigation. *Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy* 122: 565–570.

Otero-Romaní, J., Moreda-Piñeiro, A., Bermejo-Barrera, P., & Martin-Esteban, A. (2009). Ionic imprinted polymer for nickel recognition by using the bi-

functionalized 5-vinyl-8-hydroxyquinoline as a monomer: Application as a new solid phase extraction support. *Microchemical Journal*, 93(2): 225–231.

Poulin, J., Prüss-üstün, A., & Gibb, H. (2008). Mercury Assessing the environmental burden of disease at national and local levels. *Environmental Burden of Disease*, Series No. 16.

Pérez-Moral, N., & Mayes, a. . (2004). Comparative study of imprinted polymer particles prepared by different polymerisation methods. *Analytica Chimica Acta*, 504(1): 15–21.

Pichon, V., & Chapuis-Hugon, F. (2008). Role of molecularly imprinted polymers for selective determination of environmental pollutants--a review. *Analytica Chimica Acta*, 622(1-2): 48–61.

Pyreu, D. F., Ryzhakov, A. M., Kozlovskii, E. V., Gruzdev, M. S., & Kumeev, R. S. (2011). Mixed-ligand complex formation of mercury (II) ethylenediaminetetraacetate with cysteine and methionine in aqueous solution. *Inorganica Chimica Acta*, 371(1): 53–58.

Rao, M. M., Reddy, D. H. K. K., Venkateswarlu, P., & Seshaiah, K. (2009). Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste. *Journal of Environmental Management*,90(1):634–43.

Rao, T. P., Kala, R., & Daniel, S. (2006). Metal ion-imprinted polymers--novel materials for selective recognition of inorganics. *Analytica Chimica Acta*, 578(2): 105–16.

Salih, B., Denizli, a, Kavaklı, C., Say, R., & Pişkin, E. (1998). Adsorption of heavy metal ions onto dithizone-anchored poly (EGDMA-HEMA) microbeads. *Talanta*, 46(5): 1205–1213.

Sambe, H., Hoshina, K., & Haginaka, J. (2007). Molecularly imprinted polymers for triazine herbicides prepared by multi-step swelling and polymerization method. Their application to the determination of methylthiotriazine herbicides in river water. *Journal of Chromatography. A*, 1152(1-2): 130–7.

Sambe, H., Hoshina, K., Moaddel, R., Wainer, I. W., & Haginaka, J. (2006). Uniformly-sized, molecularly imprinted polymers for nicotine by precipitation polymerization. *Journal of Chromatography. A*, 1134(1-2): 88–94.

Sari, A., & Tuzen, M. (2009). Removal of mercury(II) from aqueous solution using moss (Drepanocladus revolvens) biomass: equilibrium, thermodynamic and kinetic studies. *Journal of Hazardous Materials*, 171(1-3): 500–7.

Sato et al., Mercury-removal adsorbent, method of producing mercury removal adsorbent, and method of removing mercury by adsorption, U.S.Patent 8,598,072 B2; (Dec 2013).

Singh, D. K., & Mishra, S. (2009). Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer. *Journal of Hazardous Materials*, 164(2-3): 1547–51.

Singh, D. K., & Mishra, S. (2010). Synthesis, characterization and analytical applications of Ni(II)-ion imprinted polymer. *Applied Surface Science*, 256(24): 7632–7637.

Spivak, D. a. (2005). Optimization, evaluation, and characterization of molecularly imprinted polymers. *Advanced Drug Delivery Reviews*, 57(12): 1779–94.

Sugier et al., Process for removing mercury from a gas or a liquid by absorption on a copper sulfide containing solid mass, U.S.Patent 4,094,777; (June 1978).

Thomas. F.D et al., Mercury removal in petroleum crude using H_2S/C, U.S.Patent WO/2000/069991; (June 2000).

Tom, L. A., Schneck, N. a, & Walter, C. (2012). Improving the imprinting effect by optimizing template:monomer:cross-linker ratios in a molecularly imprinted polymer for sulfadimethoxine. *Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences*, 909: 61–4.

Tuzen, M., Sari, A., Mendil, D., & Soylak, M. (2009). Biosorptive removal of mercury(II) from aqueous solution using lichen (Xanthoparmelia conspersa) biomass: kinetic and equilibrium studies. *Journal of Hazardous Materials*, 169(1-3): 263–70.

Umpleby, R. J., Baxter, S. C., Rampey, A. M., Rushton, G. T., Chen, Y., & Shimizu, K. D. (2004). Characterization of the heterogeneous binding site affinity distributions in molecularly imprinted polymers. *Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences*, 804(1): 141–9.

Wang, Y., Han, M., Liu, G., Hou, X., Huang, Y., Wu, K., & Li, C. (2015). Molecularly imprinted electrochemical sensing interface based on in-situ-polymerization of amino-functionalized ionic liquid for specific recognition of bovine serum albumin. *Biosensors & Bioelectronics*, 74: 792–798.

Wilhelm, S. M., & Bloom, N. (2000). Mercury in petroleum. *Fuel Processing Technology*, *63*(1), 1–27.

Wu, G., Wang, Z., Wang, J., & He, C. (2007). Hierarchically imprinted organic-inorganic hybrid sorbent for selective separation of mercury ion from aqueous solution. *Analytica Chimica Acta*, 582(2): 304–10.

Wulff, G., A. Sarhan., & K. Zabrocki. (1973). Enzyme-analogue built polymers and their use for the resolution of racemates. *Tetrahedron Letters* , 44, 4329-4332.

Yusof, N., Rahman, S., Hussein, M., & Ibrahim, N. (2013). Preparation and Characterization of Molecularly Imprinted Polymer as SPE Sorbent for Melamine Isolation. *Polymers*, 5(4): 1215–1228.

Zabihi, M., Haghighi Asl, a, & Ahmadpour, a. (2010). Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell. *Journal of Hazardous Materials*, 174(1-3): 251–6.

Zakaria, N. D., Yusof, N. A., Haron, J., & Abdullah, A. H. (2009). Synthesis and evaluation of a molecularly imprinted polymer for 2,4-dinitrophenol. *International Journal of Molecular Sciences*, 10(1): 354–65.

Zhai, Y., Liu, Y., Chang, X., Chen, S., & Huang, X. (2007). Selective solid-phase extraction of trace cadmium(II) with an ionic imprinted polymer prepared from a dual-ligand monomer. *Analytica Chimica Acta*, 593(1): 123–8.

Zhan, Y., Zhu, Z., Lin, J., Qiu, Y., & Zhao, J. (2010). Removal of humic acid from aqueous solution by cetylpyridinium bromide modified zeolite. *Journal of Environmental Sciences*, 22(9): 1327–1334.

Zhang, F.-S., Nriagu, J. O., & Itoh, H. (2005). Mercury removal from water using activated carbons derived from organic sewage sludge. *Water Research*, 39(2-3): 389–95.

Zhou, J., Ma, C., Zhou, S., Ma, P., Chen, F., Qi, Y., & Chen, H. (2010). Preparation, evaluation and application of molecularly imprinted solid-phase microextraction monolith for selective extraction of pirimicarb in tomato and pear. *Journal of Chromatography. A*, 1217(48): 7478–83.

Zinchenko, a a, Sakai, H., Matsuoka, S., & Murata, S. (2009). Application of DNA condensation for removal of mercury ions from aqueous solutions. *Journal of Hazardous Materials*, 168(1): 38–43.