DEVELOPMENT OF *S*-QUINOLIN-2-YL-METHYLDITHIOCARBAZATE FUNCTIONALIZED MAGNETIC NANOPARTICLES AS MAGNETIC SOLID PHASE ADSORBENT FOR THE DETERMINATION OF HEAVY METALS IN WATER SAMPLES

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by

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LIST OF SYMBOLS

M_s	Saturation magnetization
p	The equilibrium pressure of adsorbates at the temperature of adsorption
p_0	The saturation pressure of adsorbates at the temperature of adsorption
$\mathrm{p}K_a$	Negative logarithm of the acid dissociation constant
Å	Ångström = 10^{-10} m = 0.1 nm
θ	Angle
λ	Wavelength

LIST OF ABBREVIATIONS

AAS	Atomic adsorption spectrometry
APTES	(3-aminopropyl)triethoxysilane
BET	Brunauer-Emmett-Teller analysis
BJH	Barrett-Joyner-Halenda method
FESEM	Field emission scanning electron microscopy
FT-IR	Fourier Transform infrared spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limits of detection
LOQ	Limit of quantification
MNP	Magnetic nanoparticles
MNP-APTES	Silica core-shell magnetic nanoparticles
MNP-SQ2MDTC	*S*-quinolin-2-yl-methyl-dithiocarbazate functionalized magnetic nanoparticles
MSPE	Magnetic solid phase extraction
NLO	Nonlinear optical
RSD	Relative standard deviations
SPE	Solid-phase extraction
SQ2MDTC	*S*-quinolin-2-yl-methyl-dithiocarbazate
UNICEF	United Nations International Children's Emergency Fund
VSM	Vibrating sample magnetometry
WHO	World Health Organization
XRD	X-ray powder diffraction spectroscopy

PEMBANGUNAN *S*-KUINOLIN-2-IL-METILDITIOKARBAZAT BERFUNGSIKAN NANOPARTIKEL MAGNETIK SEBAGAI PENJERAP PENGEKSTRAKAN FASA PEPEJAL MAGNETIK UNTUK PENENTUAN LOGAM BERAT DI DALAM SAMPEL AIR

ABSTRAK

S-kuinolin-2-il-metilditiokarbazat berfungsikan nanopartikel magnetik (MNP-SQ2MDTC) sebagai penjerap pengekstrakan fasa pepejal magnetik (MSPE) telah dibangunkan untuk penentuan Cd^{2+} dan Cu^{2+} di dalam sampel air. Pertama sekali, permukaan MNP disalutkan dengan 3–(aminopropil)trietoksisilana (APTES) sebagai penyambung silang dan kemudian SQ2MDTC digabungkan secara kovalen pada MNP yang bersalut tersebut. Pencirian struktur dan permukaan telah dikaji menggunakan spektroskopi inframerah Fourier Transform (FTIR), spektroskopi pembelauan sinar-X (XRD), magnetometri sampel bergetar (VSM), mikroskop imbasan elektron pancaran medan (FESEM) dan analisis Brunauer-Emmett-Teller (BET). Parameter untuk MSPE telah dioptimumkan, di mana 20 mg penjerap disebarkan di dalam 25 mL sampel yang telah diselaraskan pada pH 6.0 dan disonikasikan selama 10 min, sebelum dinyahjerap di dalam 0.5 mL $HClO_4$ (1 M) dan disonikasikan selama 5 min. Dalam keadaan optimum, pengesahan kaedah yang dibangunkan ini menunjukkan lineariti yang baik dalam julat penentukuran antara 0.1–5.0 µg mL^{-1}, dengan pekali penentuan (R^2) 0.995 dan 0.996 masing-masing untuk Cd^{2+} dan Cu^{2+}. Had pengesanan (LOD) kaedah ini untuk Cd^{2+} dan Cu^{2+} ialah pada kadar 0.054 dan 0.040 µg mL^{-1}, dan had pengkuantitian masing-masing pada kadar 0.180 dan 0.134 µg mL^{-1}. Kaedah yang dicadangkan ini telah berjaya disahkan dengan penggunaan penjerap MNP-SQ2MDTC untuk penentuan Cu^{2+} dan Cd^{2+} di dalam sampel air sungai. Perolehan semula sebanyak

75.6–93.9% dan 81.5–98.7% diperolehi masing-masing untuk Cu^{2+} dan Cd^{2+}, dengan nilai sisihan piawai relatif (RSD) lebih rendah daripada 0.68% untuk kedua-dua analit. Secara keseluruhannya, penjerap MNP-SQ2MDTC yang dibangunkan mempunyai kapasiti penjerapan yang tinggi untuk akueus Cu^{2+} dan Cd^{2+}, disebabkan oleh pengkompleksan ion-ion logam pada permukaan kumpulan amino.

DEVELOPMENT OF *S*-QUINOLIN-2-YL-METHYLDITHIOCARBAZATE FUNCTIONALIZED MAGNETIC NANOPARTICLES AS MAGNETIC SOLID PHASE ADSORBENT FOR THE DETERMINATION OF HEAVY METALS IN WATER SAMPLES

ABSTRACT

S-quinolin-2-yl-methyl-dithiocarbazate functionalized magnetic nanoparticle (MNP-SQ2MDTC) as adsorbent in magnetic solid phase extraction (MSPE) was developed for the determination of Cd^{2+} and Cu^{2+} in water samples. The surface of MNP was first coated with 3-(aminopropyl)triethoxysilane (APTES) as cross-linker and then SQ2MDTC was incorporated covalently to the coated MNP. The structural and surface characteristics were investigated using Fourier Transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) spectroscopy, vibrating-sample magnetometry (VSM), field emission scanning electron microscopy (FESEM), and Brunauer-Emmett-Teller (BET) analysis. Various experimental parameters affecting MSPE such as pH, mass of adsorbent, sample volume, sonication time and type of desorption eluent had been investigated in detail to improve the extraction efficiency. The method validation under optimal MSPE conditions revealed a good linearity in the calibration range of 0.1–5.0 µg mL^{-1}, with coefficient of determination (R^2) of 0.995 and 0.996 for Cd^{2+} and Cu^{2+}, respectively. The limits of detection (LOD) of the developed method for Cd^{2+} and Cu^{2+} were found to be 0.054 and 0.040 µg mL^{-1}, and limit of quantification (LOQ) were 0.180 and 0.134 µg mL^{-1}, respectively. The proposed method has been successfully validated by applying MNP-SQ2MDTC adsorbent for the determination of the analytes in river water samples. The recoveries of 75.6–93.9% were obtained for Cd^{2+} and 81.5–98.7% for Cu^{2+} with relative standard deviations (RSD) values lower than 0.68% for both analytes. Overall, the developed MNP-SQ2MDTC adsorbent exhibited high adsorption capacity for aqueous Cd^{2+} and Cu^{2+} resulting from complexation of the metal ions to the surface of amino groups.

CHAPTER 1

INTRODUCTION

1.1 Research background

Water is one of the crucial elements which is regularly used by living organisms especially human. However, the source of clean water has depleted as many contaminations has occurred in the water body. The World Health Organization (WHO) and United Nations International Children's Emergency Fund (UNICEF) estimated that about 663 million people worldwide still lack access to safe clean water, and among these, 159 million rely on surface water (WHO & UNICEF, 2015). Thus, they are exposed to the water body which has been contaminated.

Water is mostly polluted by the anthropogenic activities which commonly deposit waste products including heavy metals. Manufacturing processes and industrial activities, especially metal smelting, electroplating and chemical industries are few sources of anthropogenic heavy metals in water (Fuge, 2013). Excessive release of heavy metals has posed a great problem globally as they do not degrade into harmless end products. The exposure caused various chronic and sub-chronic effects. For instance, millions of people in one of the most densely populated countries in the world, Bangladesh, were seriously affected by heavy metal and metalloid pollution such as As, Pb, Cd, and Cr in their water, foods and soil (Islam et al., 2018). The intensive mining and smelting activities in China which release a large amount of heavy metal waste, have caused several direct and indirect health problems to the population including children such as high cadmium level in urine, osteomalacia, arthralgia, and excessive lead in blood (Zhang et al., 2012). Several other research have reported various health problems due to the presence of heavy metals in drinking water (Jaishankar et al., 2014). Notwithstanding the fact that some heavy metals are essential for human health, negative impacts will arise if these metals are in excessive amount. Consequently, it causes toxicity to many life forms that depends on it, including human.

Over the last few decades, numerous studies were conducted and several treatment processes have been established for heavy metal removal from wastewater. These processes include membrane filtration, precipitation, adsorption, ion exchange and co-precipitation. Based on these studies, it has been discovered that the adsorption technique is the most efficient and economically feasible as a wastewater treatment operation (Burakov et al., 2018).

Adsorption technique uses adsorbent such as activated carbon, silica, alumina, bentonite and peat to bind heavy metals and further remove them from the wastewater (Crini et al., 2019). Most of these conventional materials provided low efficiency and is time consuming in removing pollutant from the wastewater (Wang et al., 2018).

Recent advancement in nanoscience and nanotechnology has shown promising potential to overcome environmental problems (Sadegh et al., 2014; Zare et al., 2013). New nanometer-sized material called magnetic nanoparticles (MNP) have developed interests in research and progression due to their unique properties. Until recently, MNP are known to be used in various fields, including cancer imaging and therapy (Bharath et al., 2019; Kang et al., 2017), tissue cryopreservation (Manuchehrabadi et al., 2017), environmental remediation (Goyal et al., 2018; Jiang et al., 2018), high density information storage (Henderson et al., 2012), electronic devices (Yang et al., 2016) and chemical catalysis (Gholinejad et al., 2018). The application of MNP for environmental remediation has captured attention as it resolves the environmental issues especially water pollution. These nanoparticles are also known to be capable of absorbing some organic and inorganic compounds (Gao et al., 2016).

An extraction approach based on magnetic or magnetizable sorbents termed as magnetic solid phase extraction (MSPE) was developed and it is suitable for the extraction of several analytes (Ding et al., 2010). This is due to their good biocompatibility, particular physical and chemical properties and high potential of applications, not only in MSPE but also in other applications such as cell separation, magnetically assisted drug delivery, enzyme immobilization, etc. (Martín et al., 2014a; Martín et al., 2014b; Shi et al., 2014). MNP are usually grafted or coated with inorganic (silica, Al_2O_3, etc.) or organic (surfactants, polymers, etc.) layers, with the aim to increase stability, avoid oxidation and formation of agglomerates that cause loss of dispersibility and magnetism (Xie et al., 2014). Besides that, specific coatings not only offer a protector function to MNP but also allow further functionalization or the establishment of successful interactions with the target analytes. The use of MNP for the development of MSPE has become increasingly popular due to the advantages of easy control and simple separation.

Dithiocarbazate and its substituted compounds remain of interest to researchers because of their wide variation in structure and properties. Some of these compounds have tunable electronic behaviour which may result in nonlinear optical (NLO) materials with unique magnetic and electrochemical properties (Bharati et al., 2013) and some demonstrate selective biological activity (Basha et al., 2012). Condensation reaction is typically used to yield substituted dithiocarbazate compounds such as *S*-benzyldithiocarbazate (SBDTC), *S*-methyldithiocarbazate (SMDTC), *S*-napthalen-2-ylmethyldithiocarbazate (SNMDTC) and S-2-picolyldithiocarbazate (S2PDTC). With the presence of nitrogen and sulphur as donors, dithiocarbazate forms chelated complexes with general formula of [M(OS)$_2$] where M can be Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+} or Pb^{2+}.

In view of the aforementioned findings, this study aims to synthesis the MNP-SQ2MDTC to be applied as sorbent for MSPE of heavy metals in environmental samples. To date, work on development of MNP-SQ2MDTC for separation and pre-concentration of Cd^{2+} and Cu^{2+} at trace levels has not been reported. The structural and surface properties of the synthesized MNP has also been investigated.

1.2 Problem statement

Research on the removal of heavy metal contaminations are still progressing and so far many adsorbents have been synthesized and are commonly used. Conventional adsorbents such as activated carbon, carbon nanotubes, silica, alumina, zeolite, bentonite, chitin and peat are found to provide low extraction capacity. Furthermore, batch adsorption method used was complicated, time consuming and used a large amount of solvent. Therefore, the quest for a simple, rapid and high efficiency of heavy metal extraction method should be initiated. Taking into account the advantages of dithiocarbazate which is able to form complexes with heavy metals, it is a promising prospect in developing MNP functionalized with the group to improve the extraction of heavy metals from water by using MSPE method.

1.3 Research objectives

The aim of this research is to develop new functionalized magnetic nanoparticles which are based on dithiocarbazate ligand. The specific objectives of this research were:

i. to synthesis and characterize MNP-SQ2MDTC adsorbent using FTIR, XRD spectroscopy, VSM, FESEM and BET analysis.

ii. to optimize MSPE parameters prior to atomic absorption spectroscopy (AAS).

iii. to validate and apply the optimized MSPE method for the determination of Cd^{2+} and Cu^{2+} in environmental water samples prior to inductively coupled plasma optical emmision spectrometer (ICP-OES).

1.4 Thesis outline

This thesis comprises of five chapters. Chapter 1 presents the research background, problem statement, and research objectives of this project. Chapter 2 is the compilation of literature review which includes the findings on heavy metal contaminants and its analysis, sample preparation methods, and the synthesis of magnetic adsorbent.

Chapter 3 provides research methodology which includes the list of chemicals and reagents used, the utilization of instrumentions, and the experimental procedures in preparing MNP-SQ2MDTC, deploying the MSPE method, the method validation, and the analysis of real samples collected.

Chapter 4 compiles the results and discussion of the whole research, which is divided into several parts. The first two parts (section 4.1 and 4.2) discusses the first objective which is the synthesis of MNP-SQ2MDTC adsorbent and also the analysis of various characterizations on the adsorbent. The second objective is explained next in two parts (section 4.3 and 4.4) which include the optimization of MSPE procedure and the validation of the method. The final section (section 4.5) covers the third objective where the application of developed adsorbent in real environmental sample is analyzed.

Lastly, Chapter 5 concludes the major findings of the study and recommendations for future studies. This chapter summarizes the overall results obtained including the optimization study, validation data and real sample analysis. Recommendations are discussed for potential improvement in related studies in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy metal contaminants

Metals that are undesirable, or in the amount that may lead to detrimental human or environmental effect, are classified as contaminants. These heavy metals are non-biodegradable and usually accumulate in living organisms, which lead to many diseases and disorders (Bailey et al., 1999). There are various sources of contamination of heavy metals which can be found mostly in industrial effluents (Barakat, 2011), military activities (Bailey et al., 1999) and vehicles emission (Manta et al., 2002).

Eventhough several heavy metals such as Fe, Cu, Zn, Co, and Se, are essential to living organisms, excessive exposure may damage the functionality of organisms. Metals such as Hg, Pb, Sn, Ni and As are generally not required for metabolic activity and are toxic at quite low concentrations (Mohammadi et al., 2014). The exposure of Hg(II) may contribute to adverse effects on central nervous system, pulmonary kidney functions and the chromosomes (Rao et al., 2009), while Pb(II) can bioaccumulate through the food chain (Qiu et al., 2008). On the other hands, prolonged inhalation of Cu(II) spray will cause an increase in the risk of lung cancer (Aydin et al., 2008).

2.1.1 Analysis of heavy metals

The awareness towards the importance of heavy metal analysis has been realized since nineteenth century, where the early study on adverse effects of heavy metals in drinking water has been reported by Wanklyn and Chapman in 1868. Since then, many powerful instruments have been developed including atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), and X-ray fluorescence spectrometry (XRF).

Atomic absorption spectrometer (AAS) is widely known as one of the common instruments used for determination of heavy metals qualitatively and quantitively. The technique has two main categories which are based on the method of atomization: flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption (ETAAS). Numerous studies employed AAS for detection of heavy metals in various matrices. Dos Santos et al., (2018) discovered an imbalance of essential metals such as Ca, Fe and Zn in Parkinson's disease patients by assessing the metal concentration in their hair through FAAS. A simple and rapid procedure which uses FAAS for determination of Fe and Zn in milk-based infant formulas was developed by Machado et al., (2016). Ivanova-Petropulos et al., (2015) utilized ETAAS to determine Pb and Cd in Macedonian white wines. Several other studies have employ AAS in their research, as listed in Table 2.1. These reported works proved that AAS is an advanced and popular instrument for heavy metal analysis.

Inductively coupled plasma (ICP) is another powerful analytical instrument for detection and measurement of heavy metals at trace level. It applies the concept of ionization of the sample by an extremely hot plasma, thus the produced elements will emit characteristic wavelength specific light which can then be measured by the detector. ICP is typically coupled with optical emission spectrometry (OES) and mass spectrometry (MS) detector. The application of ICP has been reported in several studies (Table 2.2). Baseri et al. (2017) used ICP-OES to determine the potential health risks of trace metals including Pb, Cd, Ni, Fe, Sn, Zn, Cr, and Cu in cheese to consumers. Huseyinli et al. (2016) monitored the concentration of heavy metals such as Cr, Cu, Fe, Pb, Co, Ni, and Cd in the drinking water of Oguz – Gabala Baku pipeline by employing ICP-MS technique. ICP-MS also was applied to determine metal ions like Cd, Hg, and Pb in nail polish (Huang et al., 2018).

Table 2.1: Recent application of AAS for detection of heavy metal ions

Metal ion	Source	Technique	LOQ	Reference
Ca, Fe, Zn	Hair of Parkinson's Disease (PD) patients	FAAS	36 µg g^{-1} for Ca, 22 µg g^{-1} for Fe, 32 µg g^{-1} for Zn	(dos Santos et al., 2018)
Fe, Zn	Milk-based infant formulas	FAAS	—	(Machado et al., 2016)
Pb, Cd	Macedonian wine	ETAAS	0.40 µg/L for Cd 5.60 µg/L for Pb	(Ivanova-Petropulos et al., 2015)
Cd, Cr	Yerba mate plant	GF-AAS	8.4 ng g^{-1} for Cd 23.9 ng g^{-1} for Cr	(Borges et al., 2017)
Cd, Cr, Pb	Ceramic tableware	GF-AAS	0.21 µg g^{-1} for Cd, 1.50 µg g^{-1} for Cr, 3.00 µg g^{-1} for Pb	(Oreste et al., 2019)
Pb, Cd, Cr, Ni, Mn, Zn, Fe	Salt lake water and therapeutic mud	FAAS and GF-AAS	—	(Radulescu et al., 2015)
Cu, Cr, Cd, Pb	Brazillian yogurt	ETAAS	1.4 ng g^{-1} for Cd, 8.3 ng g^{-1} for Cr, 16.3 ng g^{-1} for Cu, 35.4 ng g^{-1} for Pb	(de Andrade et al., 2018)
V, Ni, Fe	Fuel fly ash	GF-AAS	47.53 ng for V, 2.23 ng for Ni, 15.00 pg for Ga, 10.30 ng for Fe	(Cárdenas Valdivia et al., 2018)
Hg	Sea water and river water	ETAAS	0.084 µg L^{-1}	(López Guerrero et al., 2017)
Pb	Whole blood	ETAAS	0.4 ng mL^{-1}	(Alavi et al., 2017)
Mn, Cr, Cd, Pb	Kulufo River, Arbaminch, Gamo Gofa, Ethiopia	FAAS	—	(Tsade, 2016)
Pb	Road dust	GF-AAS	0.07-2.20 mg kg^{-1}	(Fick et al., 2018)
Cd, Pb	Organic pharmaceutical formulations	GF-AAS	13 ng g^{-1} for Cd 165 ng g^{-1} for Pb	(Aleluia et al., 2017)

Table 2.2: Application of ICP for detection of heavy metal ions

Source	Technique	Metal ion	LOD	Reference
Iranian cheese	ICP-OES	Cd	0.049 µg kg^{-1}	(Baseri et al., 2017)
		Pb	2.000 µg kg^{-1}	
		Ni	0.290 µg kg^{-1}	
		Cr	0.096 µg kg^{-1}	
		Cu	0.300 µg kg^{-1}	
		Sn	0.161 µg kg^{-1}	
		Fe	0.160 µg kg^{-1}	
		Zn	0.270 µg kg^{-1}	
Drinking water from Oguz – Gabala Baku pipeline	ICP-MS	Al, Cr, Cu, Fe, Pb, Co, Ni, As, Cd	—	(Huseyinli et al., 2016)
Nail polish	ICP-MS	As	0.06 ng g^{-1}	(Huang et al., 2018)
		Cd	0.12 ng g^{-1}	
		Sb	0.14 ng g^{-1}	
		Hg	0.20 ng g^{-1}	
		Pb	12.00 ng g^{-1}	

The studies on heavy metals can also be conducted by using x-ray fluorescence spectrometer (XRF). IUPAC defines XRF analysis as “a kind of analysis based on the measurement of the energies and intensities of characteristic X-radiation emitted by a test portion during irradiation with electromagnetic radiation” (McNaught & Wilkinson, 1997). XRF technique has been operated to measure heavy metals in air (Talbi et al., 2018), soil (Hu et al., 2017), pulverized coal (Yan et al., 2016) and even in consumer products such as container bottle (Turner, 2019) and plastic toys (Ratnakumar et al., 2017). It is expected that the application of these instruments will be widen in the future and become one of the important chemical analysis tools.

2.2 Sample preparation method

Regardless of the development of highly efficient analytical instrumentations for determination of targeted analytes in samples, most of them cannot handle the matrix directly. In addition, low concentration of analytes is also a challenge in the analysis (Faraji et al., 2010).

Fortunately, these limitations can be solved by employing sample preparation procedures like preconcentration–separation technique prior to instrument analysis. Methods such as ion exchange, liquid-liquid extraction (LLE), cloud point extraction, and solid phase extraction (SPE) are commonly used pre-treatment methods for heavy metals determination combined together with other analytical instruments. These methods are able to enhance sensitivity and overcome issues like matrix interference.

2.2.1 Ion exchange

The ion exchange technique is applied in various applications for the preconcentration of trace heavy metal ions. Chen et al. (2017) managed to remove Pb^{2+}, Cd^{2+}, and UO_2^{2+} from water by exchanging the ions with tetramethylammonium (TMA) cations inside the interlayer space of the newly developed two-dimensional layered silicate RUB-15. Wang et al. (2014) developed a novel potential-responsive hybrid film system composed of polyaniline and layered α-zirconium phosphate nanosheet which is able to exchange metal ions like Ni^{2+}, Cd^{2+}, and Pb^{2+}. Ion exchange has been used as one of the adsorption modes, together with coordination to adsorb Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} and Cr^{3+} ions using the new reduced graphene oxide grafted by 4-sulfophenylazo groups (RGOS) adsorbent (Zhang et al., 2018). The results of these studies are summarized in Table 2.3.

Table 2.3: Summary of results of several reported studies which using ion exchange method

Adsorbent	Analytes	Maximum adsorption capacity (mg/g)	Reference
Layered silicate RUB-15	UO_2^{2+}	152	(Chen et al., 2017)
	Pb^{2+}	338	
	Cd^{2+}	190	
α-ZrP/PANI hybrid films	Pb^{2+}, Cd^{2+}, Ni^{2+}	—	(Wang et al., 2014)
Reduced graphene oxide grafted by 4-sulfophenylazo groups (RGOS)	Pb(II)	689	(Zhang et al., 2018)
	Cu(II)	59	
	Ni(II)	66	
	Cd(II)	267	
	Cr (III)	191	

Due to numerous advantages of ion exchange technique such as high ion selectivity, pH independence, reusability and regeneration capability of ion-exchange material (Bashir et al., 2018), it is commonly applied for heavy metal removal. Different types of substances can be used as the ion-exchange material, including inorganic, organic and composite (Naushad et al., 2015). Knöll and Seubert (2012) also asserted that large injection volumes can be employed through ion exchange chromatography, thus the improvement of detection limits can be achieved. Nevertheless, the technique has difficulties in treating a large amount of effluent as it requires high-cost ion exchange technology. Thus, it is not suitable to be applied in large and industrial scale.

2.2.2 Liquid-liquid extraction

When two immiscible liquid phases with different dissolved components is in contact, the components will transfer and their ratio will be distributed, hence the separation of targeted elements is possible. The technique which uses this concept is known as liquid-liquid extraction (LLE). This method is usually employed as an alternative method when other techniques such as distillation, evaporation, and crystallization, are incapable to do the desired separation (Amani et al., 2018).

Since introduced in 1907 for the petroleum industry (Hutton & Holland, 1972), liquid-liquid extraction has become one of the most popular methods for extraction. It has been applied for determination of pesticide (Fang et al., 2017; Farajzadeh et al., 2019), marine toxins (Wunschel et al., 2018), ionic dyes (Bukman et al., 2017) and phenolic compounds (Jiao et al., 2015; Tabaraki & Heidarizadi, 2019).

Heavy metals can also be determined and separated using LLE method. Wei et al. (2016) used the technique to selectively recover Au(III), Pt(IV), and Pd(II) from aqueous solutions. Mane et al. (2016) separated chromium (VI) from alloys and tannery industries effluent effectively. One of the rarest naturally occurring transition metal elements, rhenium, has been successfully recovered from acidic chloride solution by Srivastava et al. (2015).

Eventhough LLE is a traditional technique for product purification and material recovery, the long list of its advantages has made it commonly chosen as a separation technique. The simple method has high extraction selectivity and provides a high degree of sample clean-up (Płotka-Wasylka et al., 2016). In addition, Panigrahi et al. (2016) stated that LLE is the most effective technique for metal ion enrichment. The claim is supported by Béni et al., (2019), where they asserted that LLE is one of the most powerful and low-cost method for chromium ions separation. They also mentioned that numerous analytical instruments can be easily coupled with LLE. It is also an energy-wise alternative for the metal extraction which requires extremely high energy (Panigrahi et al., 2016).

LLE is not preferable for green technology and solution as it produces large volume of aqueous waste and toxic solvent that might contribute to pollution (An et al., 2017; Panigrahi et al., 2016; Shah et al., 2011). LLE is also tedious and time-consuming, with possible formation of emulsion that limits the efficiency of the extraction (Bukman et al., 2017; Płotka-Wasylka et al., 2016). Due to aforemention reasons, researchers start to opt for the other better methods.

2.2.3 Cloud point extraction

Cloud point extraction (CPE) was developed as an alternative method to the conventional liquid-liquid extraction (Ojeda & Rojas, 2012). CPE is a method which is based on the phase separation that occurs in aqueous solutions of non-ionic surfactants and zwitter ionic surfactants when the heat is increased above the cloud point temperature.

CPE is usually chosen compared to LLE due to the fact that it offers a “greener” chemistry and more environmentally friendly. It replaces the generally toxic organic solvents with low toxicity surfactants and requires a small amount of the solvent (Shah et al., 2011). Furthermore, the surfactants used are non-flammable and have low volatility, thus lowering the safety risk during extraction process (Ojeda & Rojas, 2012). Additionally, Pytlakowska et al. (2013) emphasized on the distinct merits of CPE where it offers simplicity, inexpensive, and has high ability to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors.

Recently, CPE has been commonly applied to extract and preconcentrate a wide range of metal ions from aqueous solutions. The CPE method has been used for the determination of trace V(V) and V(IV) in edible vegetable oils and vinegar with a recovery rate in the range of 91-98% (Temel et al., 2019). Dissolved iron in produced water from the petroleum industry has been successfully quantified using the CPE procedure with recovery of 103.28% (Gondim et al., 2017). Shah et al. (2019) applied the CPE method with bis[(2-acetyl pyridine) 4-phenyl 3-thio-semicarbazone (APPT) solution as the complexing reagent to determine Co^{2+}, Ni^{2+} and Cu^{2+} ions in water samples.

In spite of that, Peng et al. (2015) cast doubt on the hydrophobic interaction between the solutes and surfactant, where other hydrophobic species may also be extracted and interfere the analysis of the targeted elements. They also claimed that the CPE method is usually incompatible with ICP-MS analysis as the surfactant phase obtained is viscous and dilution with organic solvent is required. Moreover, the stability of ICP will be affected due to the deposition of carbon particles at the mouth of the torch tube. Ghasemi & Kaykhaii (2017) also argue that the heating step to increase the temperature above the cloud point temperature would be time consuming.

2.2.4 Solid-phase extraction

Solid-phase extraction (SPE) is a separation technique in which a solid phase is in contact with dissolved analytes in a matrix and retained due to the interactions with the sorbent. It is the most extensively used sample pretreatment method (Li et al., 2017).

The development of SPE has improved in various form of sorbents including in the shape of disks, cartridges and well plates.

SPE is a powerful tool for the separation and preconcentration of various organic and inorganic analytes (Saçmaci et al., 2011). SPE is preferrable because it has impressive merits such as low consumption of hazardous organic solvents, simplicity of the pretreatment procedure, high enrichment and recovery, rapid, sensitive and environmentally friendly (Bagheri et al., 2012; Daşbaşi et al., 2015; Xu et al., 2012). SPE is applied in different types of matrices such as sediments, activated sludge, soil, biological fluids, drug formulations, detergent, plant, food and beverages (Kraševec & Prosen, 2018; Wells, 2013).

SPE is considered as a better alternative as it addressed most of the drawbacks encountered by LLE. A summary of the comparison between SPE and LLE is outlined in Table 2.4 (Abd-Talib et al., 2014; Płotka-Wasylka et al., 2015; Rodríguez et al., 2016).

Regardless of the massive advantages it offers, there are plentiful drawbacks of using SPE method. Conventional SPE needs the sorbent to be packed into the costly column and it may lead to problems such as column blockage and high back pressures concerning small particle size-packing (Hemmati et al., 2018; Yavuz et al., 2018). In addition, the extraction at low concentration level and complex matrices limits the efficiency of SPE (Li et al., 2017). Several steps including activation of the SPE column, sample elution and elution evaporation may increase the operation time (Pang et al., 2019; Yavuz et al., 2018).

Table 2.4: Comparison between liquid-liquid extraction (LLE) and solid-phase extraction (SPE)

Feature	liquid-liquid extraction (LLE)	solid-phase extraction (SPE)
Solvent volume	Large amount	Small amount
Solvent purity	High purity solvent is required	Low purity solvent still gives good result
Sample volume	Limited	High
Enrichment factor	High	Very high
Solute limitation	Polar compound	None
Waste generation	Large amount and toxic	Few
Durability	Low – single or several times use only	Highly durable – reusable
Duration	Long time	Short time

Consequently, a great deal of research into the enhancement of extraction performance and solving the extraction problems has been performed, which has led to the development of simplified methodologies such as magnetic solid phase extraction (MSPE).

2.2.5 Magnetic solid phase extraction

Magnetic solid phase extraction (MSPE) is a new derivative of SPE which is based on the use of magnetic sorbents. It is the combination of magnetic inorganic material with non-magnetic adsorbent material (Han et al., 2012). MSPE is a magnetically assisted chemical separation, which uses magnetized particles in nano or micron size as adsorbent (Rodriguez et al., 2010). MSPE was pioneered by Šafaříková and Šafařík in 1999 where they used the method to separate reactive copper phthalocyanine dye from water sample. Since then, it has attracted great a deal of research interest due to its vast advantages including ease of automation, high extraction efficiency, and rapid phase separation (Aliyari et al., 2016). Rodriguez et al. (2010) also asserted that the method is easier, environmentally friendly and low cost.

MSPE is conducted by dispersing the magnetic nanoparticle adsorbents into the sample for a period of time before they are separated from the liquid phase by an external magnetic field. Then, the analytes are desorbed from the recovered adsorbent by elution with appropriate solvent and analyzed. No costly instrument or any type of device including column and cartridge is needed to operate MSPE, making it time-effective and easy to operate (Diniz & Tarley, 2015; Vasconcelos & Fernandes, 2017). MSPE does not require any centrifugation or filtration to isolate target analytes from aqueous medium, unlike conventional SPE, hence makes the method simpler and easier (Yavuz et al., 2018). Hemmati et al., (2018) added that the simplicity of MSPE allows sample to be less manipulated and produce high quality of outputs. Dispersion of nano-sized adsorbent in the matrix allows a sufficiently large contact area between the sorbents and the analytes, hence rapid mass transfer is achieved, and high extraction efficiency is ensured (Ding et al., 2010; Han et al., 2012).

Moreover, MSPE is widely used for preconcentration of organic pollutants and inorganic metal chelates (Diniz & Tarley, 2015) and can be directly applied to the samples containing microorganisms and particles that are commonly found in environmental and biological matrices (Ding et al., 2010). Furthermore, the magnetic nanoparticles used in MSPE are recyclable and reusable, hence economically favorable (Li et al., 2016).

Due to the easy modification of the MNP surface with different functional molecules or groups, the functionalized MNP can be used as adsorbent of specific analytes hence turned MSPE to a highly selective extraction (Shi et al., 2014). Throughout two decades since its inception, numerous MSPE sorbents have been developed and successfully applied in various matrices which include food (Barreto et al., 2018; Xia et al., 2017), marine biota (Mehdinia et al., 2017), plants (Yin et al., 2016) and biological samples (Sun et al., 2015). Table 2.5 summarizes the recent development of heavy metal sorbent for heavy metal analysis in a period of five years.

By considering all of mentioned merits and significant advantages, it can be concluded that MSPE is a prospective technique for sample pretreatment and boosts the development in separation science.

Table 2.5: Application of MSPE sorbent for heavy metal analysis

MSPE sorbent	Instrument	Analyte	LOD (ng mL^{-1})	Sample matrix	Reference
Ni–Al LDH/Fe_3O_4	FAAS	Mn(VII)/Mn(II)	0.1	Water	(Abdolmohammad-Zadeh et al., 2019)
γ-Fe_2O_3@*C. micaceus*	ICP-OES	Co(II) and Hg(II)	0.017-0.04	Water and food	(Özdemir et al., 2019)
Fe_3O_4@catechol	FI-ICP-OES	Co(II), Cu(II), Pb(II), Cd(II), Ni(II), Cr(III) and Mn(II)	0.2–0.9	Water and fruit	(Yamini & Safari, 2018)
Fe_3O_4@PDA	FAAS	Cu(II)	220	Food	(Yavuz et al., 2018)
Fe_3O_4/HAP/GQDs	ICP-AES	Cu(II)	0.58	Food	(Sricharoen et al., 2017)
Fe_3O_4@MnO_2,Al_2O_3	ICP-OES	Cr(III)	20 (ng L^{-1})	Water	(Mononde et al., 2017)
$MnFe_2O_4$-Takovite	FAAS	Pb(II)	0.67	Water and food	(Kardar et al., 2016)
DMG-C_{16}MIM/MGO	FAAS	Ni(II)	160	Food, beverages, and cigarette	(Aliyari et al., 2016)
Fe_3O_4@SiO_2@Polypyrole	FAAS	Cd(II), Ni(II)	0.3–1.2	Seafood	(Abolhasani et al., 2015)
HNT–Fe_3O_4	FAAS	Cd(II)	0.27	Water and biological	(Amjadi et al., 2015)
L-NH2@SiO2@MNP	FAAS	Cd(II)	0.11	Water and soil	(Sharma et al., 2014)
Py-Fe_3O_4@MCM-41	FAAS	Pb(II), Cu(II)	0.08–0.1	Fuel products	(Behbahani et al., 2014)

2.3 Synthesis of magnetic adsorbent

2.3.1 Magnetic nanoparticles

As defined by IUPAC, nanoparticle is molecule with dimensions in the 1–100 nm range (Vert et al., 2012). Nanoscale particles are small enough that their optical and electrical properties, as well as hardness, toughness, and melting point, can differ markedly from the properties exhibited by macroscopic particles of the same materials (Theodore & Kunz, 2005). The unique properties of nanoparticles have developed interests in research and progression in discovering and widening their application.

Furthermore, nanoparticle can be manipulated with the addition of magnetic core to produce more powerful adsorbent called magnetic nanoparticles (MNP). MNP are commonly composed of magnetic elements, such as iron, nickel, cobalt and their oxides like magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), cobalt ferrite (Fe_2CoO_4), chromium dioxide (CrO_2). All ferrites are metal oxides, which means their surface is covered with abundance of hydroxyl groups. This properties enables growing of well-defined shells of different materials around the ferrite core or, when functional materials are targeted, grafting functional groups suitable for the supporting of all kinds of actuators, ligands and/or catalysts by covalent bonds (Riente et al., 2011).

MNP can be synthesized chemically, physically and biologically, but the most common is the chemical methods (Ali et al., 2016; Rasheed & Meera, 2016). Numerous methods developed for synthesizing MNP including co-precipitation, hydrothermal, microemulsion, sonochemical, thermal decomposition, electrochemical decomposition, microwave-assisted, solvothermal, chemical vapor deposition, combustion, carbon arc, laser pyrolysis, mycosynthesis and microorganism biosynthesis. The type of method used to synthesis MNP usually depends on their intended purpose and eventual application (Ansari et al., 2019). Above all, co-precipitation method is the most popular choice to synthesis MNP, substantially because of its simplicity and low risk (Indira & Lakshmi, 2010). Generally, co-precipitation is conducted in inert nitrogen atmosphere, and other parameters such as reactant concentration, type of salts, pH and ionic strength will give different features of size, shape, and magnetic properties of the synthesized MNP (Lassoued et al., 2017).

Researchers have discovered recently that several nanoparticles can be used as heavy metals removal due to the easy modification of their surface functionality and their high surface area-to-volume ratio which can increase adsorption capacity and efficiency (Priester et al., 2012). These include MNP which have the advantages of both magnetic separation techniques and nano-sized materials. The magnetic nanoadsorbents can be easily manipulated and recovered from aqueous solutions under an external magnetic field due to their magnetic property (Bagheri et al., 2012). Hence, they have the advantages of simplicity, sensitivity, and easy to operate in adsorption process (Li et al., 2011; Peng et al., 2010). They also have potential to be used as a reusable adsorbent under appropriate conditions (Priester et al., 2012).

In addition, MNP exhibit the phenomenon of superparamagnetism which is a behaviour of individual particles become magnetized only when exposed to an external magnetic field, but exhibit no remanent magnetization when the field is removed (Vatta et al., 2006). Definitely by having this characteristic, MNP will obtain an extra benefit of minimizing risk of particle aggregation (Martín-Saavedra et al., 2010). The improved efficiency of this material in removing metal ions, inexpensiveness and the possibility for scaling-up its production to industry indicate the high practical impact and environmental importance of this adsorbent (Kyzas & Matis, 2015).

2.3.2 Methyldithiocarbazate ligand

The synthesis of new coordination compounds which have nitrogen and sulphur donor atoms has been in the spotlight in recent times. Dithiocarbazate is one of the compounds which receives great attention due to its remarkable characteristics including biological, physicochemical, and optoelectronic properties. Dithiocarbazates which have primary amine at the terminal can also formed Schiff bases when reacted with aldehyde or ketone. Dithiocarbazate compounds are used to apply as antibacterial (Bhat & Kumar, 2019), antioxidant (Sarhan et al., 2019), antimicrobial (Zangrando et al., 2017) and antitumor (Adly & El-Shafiy, 2019) agents.

Dithiocarbazates exist in two tautomeric forms, thione (C=S), and thiol (C–S). The thiol structure is usually favorable over thione group as thione relatively unstable in the monomeric form. The alteration of the properties of related ligands and their metal complexes is possible by introducing different substituents (Manan et al., 2012; Takjoo & Centore, 2013).

S-alkyl dithiocarbazate which also constitute one of the most important classes of mixed hard–soft nitrogen–sulfur donor ligands has been extensively studied. The possession of both hard nitrogen and soft sulfur donor atoms on the compound is important as it acts as bidentate-chelate through coordination with vast array of transition and non-transition metal ions (Takjoo et al., 2011). Besides, two out of four potential donor atoms are sterically available at a time to chelate with metal ions (Zangrando et al., 2015). Chen et al. (2011) added that the coordination complexes formed is stable and has intense color.

Furthermore, dithiocarbazates also have a high affinity towards heavy metal cations and in aqueous solutions, their chelates are remarkably stable (Girginova et al., 2010). Another interesting fact is that *S*-methyl dithiocarbazate is the first hydrazine derivative for which different conformers have been found in the solid state, in solution, and in transition metal complexes (Mattes & Weber, 1980).

S-quinolin-2-yl-methyldithiocarbazate (Figure 2.1) is one of the *S*-alkyl dithiocarbazate which was studied by How et al. (2007). This substituted dithiocarbazate has the same properties as most other dithiocarbazate derivatives which has high affinity towards heavy metal ions and ability to chelate and form complex with the ions. Hence, it will be an intriguing prospect to attach this ligand on MNP and applied as absorbent for heavy metals removal.

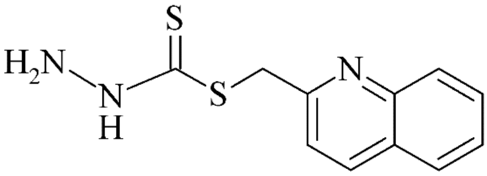

Figure 2.1: Chemical structure of *S*-quinolin-2-yl-methyldithiocarbazate

2.3.3 MNP functionalized with dithiocarbazate ligand

The synthesis of magnetic nanoparticles functionalized with dithiocarbazate ligand has never been reported. However, there are several literatures on functionalizing MNP with other ligands. Lee et al., (2014) coated MNP with a synthetic ligand called *bis*-Zn-DPA for clearing bacteria and endotoxin from the bloodstream. Iron oxide nanoparticles has been attached with a metal-binding organic ligand, ethylenediaminetetraacetic acid (EDTA) to remove Cd^{2+} and Pb^{2+} from contaminated water (Huang & Keller, 2015). A new catalyst for the oxidation of alkanes has been developed by Azarkamanzad et al., (2019) who supported Fe_3O_4 nanoparticles with $[Co(2,4,6\text{-tris(2-pyridyl)-1,3,5-triazine})Cl_2]\cdot 2H_2O$ metal complex.

Dithiocarbazate showed a great potential as heavy metal separator. It can form complex with broad variety of heavy metal ions, including Ni, Zn, Pb, Pd, Co, Fe, Mn, Cu and Cd (Alshaheri et al., 2017; Bsegum et al., 2017; Lima et al., 2018; Takjoo et al., 2018). Due to tautomer between thione and thiol in *S*-substituted dithiocarbazates compounds, N and S donor atoms are bonded to the metal ion with the formation of five- or six-membered rings (Takjoo & Centore, 2013). The coordination ability of the ligand will be increased if there are presence of additional donor atoms in suitable position in the compound, giving risse to different coordination geometries (Takjoo et al., 2011). The dithiocarbazate-metal complex formed will have different geometric, electronic, optical (Bera & Seok, 2010), magnetic (Liu et al., 2009), semiconducting (Bera et al., 2010) and radiopharmaceutical properties (Boschi et al., 2010).

Based on all the facts given, it is anticipated that the MNP-dithiocarbazate developed in this study will be successfully developed and able to form complex with metal ions, hence separating them from medium tested that is water.