



CHAPTER II

THEORY AND LITERATURE REVIEW

This chapter covers the principle of solid-phase extraction (SPE), its mechanism and the type of solid support. Knowledge of silica and the procedure of functionalization are also described. Furthermore, the sample preparation for metal analysis was also explained. In the final part, the information on doping molecules and their literature review were described.

2.1. Solid-phase extraction [20-21]

2.1.1. Principle

Solid-phase extraction (SPE) is the most important technique used in sample preparation. SPE can be used in a fashion similar to liquid-liquid extraction (LLE). SPE has a number of advantages over LLE. It reduces solvent usage and exposure, disposal cost and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and trace determination of metal ions.

The principle of SPE is similar to that of LLE, involving partitioning of solutes between two phases. However, instead of two immiscible liquid phase, as LLE, SPE involves partitioning between liquid (sample matrix) and solid (sorbent) phases. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retain the analytes. After all of the sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent. Presently, its use is intended to achieve some or all of these three objectives:

- 1) Preconcentration of analytes
- 2) Removal contaminants from the sample (clean up)
- 3) Removal of the sample matrix/solvent exchange.

In case of metal extractions, the amount of metal ion on the adsorbents and the distribution ratio of the metal were calculated according to the following equations [22].

$$q = (C_i - C_e) \times L/W \quad (2.1)$$

$$D = q/C_e \quad (2.2)$$

Where	q	is the amount of metal on the adsorbents (mol/kg)
	D	is the distribution ratio of the metal (L/kg)
	C _i	is the initial metal concentration in the aqueous solution (mol/L)
	C _e	is the metal concentration in the aqueous solution at equilibrium (mol/L)
	L	is the volume of the aqueous solution (L)
	W	is the weight of the adsorbents (g)

2.1.2. Mechanism of solid-phase extraction [20-21]

Mechanism of SPE can be divided into four classes: normal phase, reversed phase, ion exchange and adsorption. Normal phase SPE typically involve a nonpolar matrix and a polar stationary phase. Retention of an analyte under normal phase conditions is primarily due to interactions between polar functional groups of the analyte and polar groups on the sorbent surface. These include hydrogen bonding, π - π interactions, dipole-dipole interaction and dipole-induced dipole interactions.

Reversed phase separation involves a polar or moderately polar sample matrix and a nonpolar stationary phase. Retention of organic analytes from polar solution onto these SPE materials is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the silica surface. These nonpolar-nonpolar attractive forces are commonly called van der Waals forces or dispersion forces.

Ion exchange SPE can be used for charged compounds in a solution. The primary retention mechanism of the compound is based mainly on the electrostatic attraction of the charged functional group on the compound to charged groups that are bonded to the silica surface. Ion exchange sorbents have either cationic or anionic functional groups and when in the ionized form attract compounds of the opposite charge. A cation exchange phase will extract an analyte with a positive charge and vice versa.

In separation involving adsorption, solute and mobile-phase molecules compete for active sites on the surface of the solid stationary phase. Interaction

between solute and mobile phase was hydrophobic or hydrophilic depending on solid support.

2.1.3. Type of solid support

Two categories of solid supports, organic and inorganic materials, are used in SPE. Organic sorbents include polystyrene-divinylbenzene, graphite carbon and activated carbon. Typical inorganic supports are silica (SiO₂)_n, alumina (Al₂O₃) and magnesium (MgSiO₃ or Florisil). Among these materials, silica gel is the most widely used due to its thermal stability and high mechanical strength. Furthermore, modification of silica surface to enhance its selectivity is facile comparing to other materials. Accordingly, the functionalization of silica for a desired application became an interesting target for the development of extractive materials.

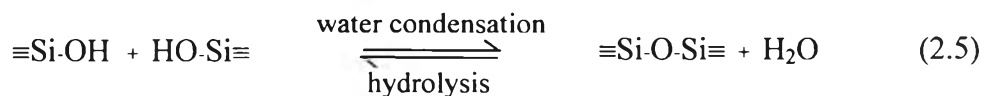
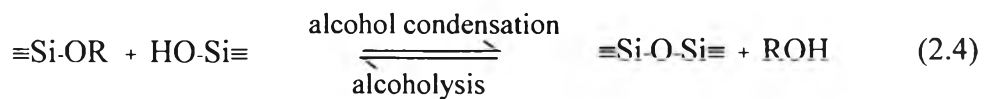
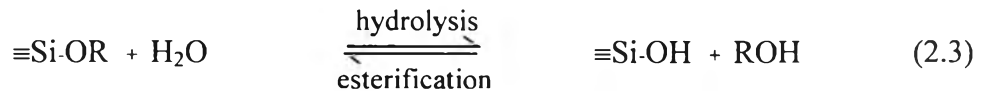
2.2. Silica

2.2.1. General

Silica is an inorganic polymer with the general structural formula of (SiO₂)_n. Typically, silica can be classified according to IUPAC in three types depending on its pore size [23].

1. Microporous silica with pore diameter smaller than 2 nm.
2. Mesoporous silica with pore diameter between 2 and 50 nm.
3. Macroporous silica with pore diameter larger than 50 nm.

Silica was usually made by acidification of sodium silicate or polymerization of silicic acid. Also, this material could be synthesized via sol-gel process as written in equations 2.3-2.5.



The silica which is used in most chromatographic applications and in typical SPE procedure is an amorphous porous solid with surface area of 50-500 m²/g and pore diameter of 50-500 Å. The primary advantages of silica are its availability in a wide range of well-defined surface area and pore size as well as its relatively low cost.

The silica particles contain unreacted silanols and siloxanes. The silanols are considered to be strong adsorption sites, while the siloxanes are hydrophobic. Silanols on the surface may be single, geminal or vicinal in form (Figure 2.1).

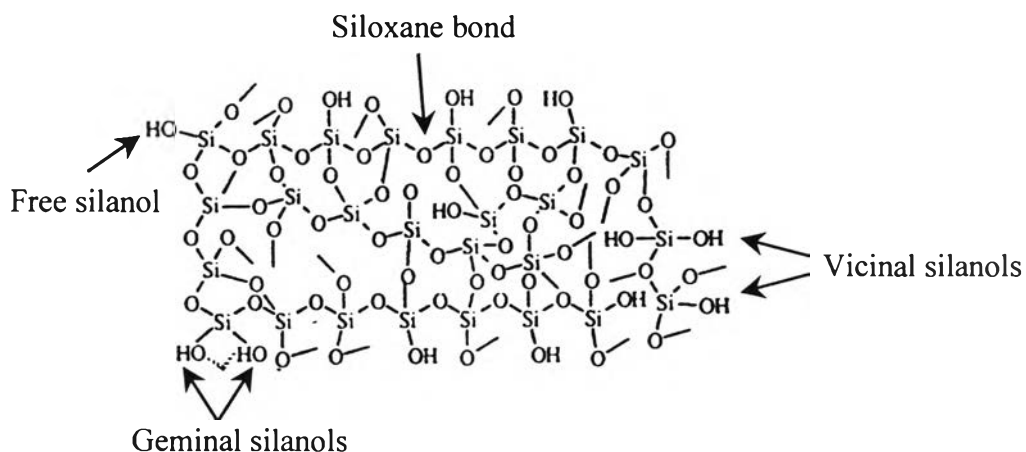


Figure 2.1 Structure of a silica gel showing siloxane bond, single free silanol, geminal silanols and vicinal silanols [24]

The silanol groups present on the silica surface have an acidic character, which the reaction is displayed as follows.



The pKa value of this reaction is about 6.8 ± 0.5 [25]. In addition, the acidic character of surface silanols confirms some ion-exchange properties on porous silica. The ion-exchange properties of silica are highly dependent on silanols concentration, surface area and pH of solution. Typically, silica has a surface charge character as shown by the following equations.



Another physical properties of silica are isoelectric point and point of zero charge. The isoelectric point is the pH at which there are no charges outside the silica surface, whereas the point of zero charge is the pH at which no acid or base is consumed in generating a surface charge. The isoelectric point and the point of zero charge of silica are about 2.5 and 2, respectively [26].

2.2.2. Functionalization of silica

Three techniques are used for the functionalization of organic compounds on the surface of silica: chemical derivatization, impregnation and doping techniques [8]. In the first technique, a chemical bond is formed between the active sites on the

surface of silica and those of the organic compounds. Advantage of this technique is the high stability of the chemical bond, but the preparation is very complicated and time-consuming. Moreover, the chelating agents that can be bond to silica gel are limited. In the second technique, the organic compounds are directly adsorbed on the silanol groups of the silica gel surface by soaking the adsorbent in the reagent solution, which after drying give a support coated in reagent. The technology is highly versatile and a large variety of reagents have already been loaded on silica. However, the adhesion of the reagent to the support is rather weak and leaching is frequently observed. Consequently, the lifetime of the support is short. In the last case, the doping technique is gaining popularity for the immobilization of organic compounds in organic matrices due to its high versatility. This technique is the direct encapsulation of organic molecules by using sol-gel process. The derivatization of the chemical reagent is not required prior to the encapsulation step and thus reactivity and specificity of the dopant are generally maintained.

2.3. Mesoporous silica

The discovery by Mobil researchers [27] of the M41S family of mesoporous molecular sieves with pore size from 1.5 to 10 nm has stimulated interest in the potential use of these materials as catalysts, adsorbents and advanced materials [28-30]. These materials have very high surface area ($> 1000 \text{ m}^2/\text{g}$), ordered pore structure and extremely narrow pore size distribution. Mesostructure syntheses rely on surfactant micelles or liquid-crystal arrays of micelles as structure-directing agents (templates) for the assembly and subsequent polymerization of inorganic precursors at the surfactant-solution interface. Depending on the synthesis conditions, the obtained materials consisted of three different members: a hexagonal phase MCM-41, a cubic phase MCM-48, or a non-stable lamellar phase MCM-50. A number of mechanistic models have been proposed to explain the formation of mesostructure.

Beck *et al.* [31] proposed a liquid crystal templating (LCT) mechanism that the structure is defined by the organization of surfactant molecules into liquid crystals which serve as templates for the formation of MCM-41 structure. Two possible mechanism pathways were included in this type of mechanism. The first step in the synthesis would correspond to the formation of a micellar rod around the surfactant micelle which in a second step will produce a hexagonal array of rods followed by the

incorporation of an inorganic array (silica, silica-alumina) around the rodlike structures (Figure 2.2).

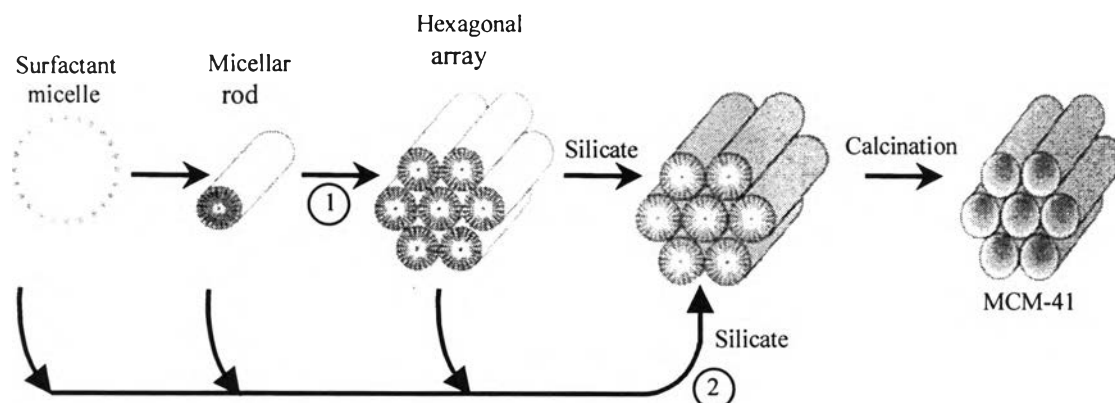


Figure 2.2. Two possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal initiated and (2) silicate anion initiated [31]

Davis *et al.* [32], by carrying out in situ ^{14}N NMR spectroscopy, concluded that the liquid crystalline phase is not present in the synthesis medium during the formation of MCM-41, and consequently, this phase cannot be the structure-directing agent for the synthesis of the mesoporous materials in agreement with the already proposed mechanism through route 2. Thus, the randomly ordered rodlike organic micelles interact with silicate species to yield two or three monolayers of silica around the external surface of the micelles. Subsequently, these composite species spontaneously form the long-range order characteristic of MCM-41. The mechanism is illustrated in Figure 2.3.

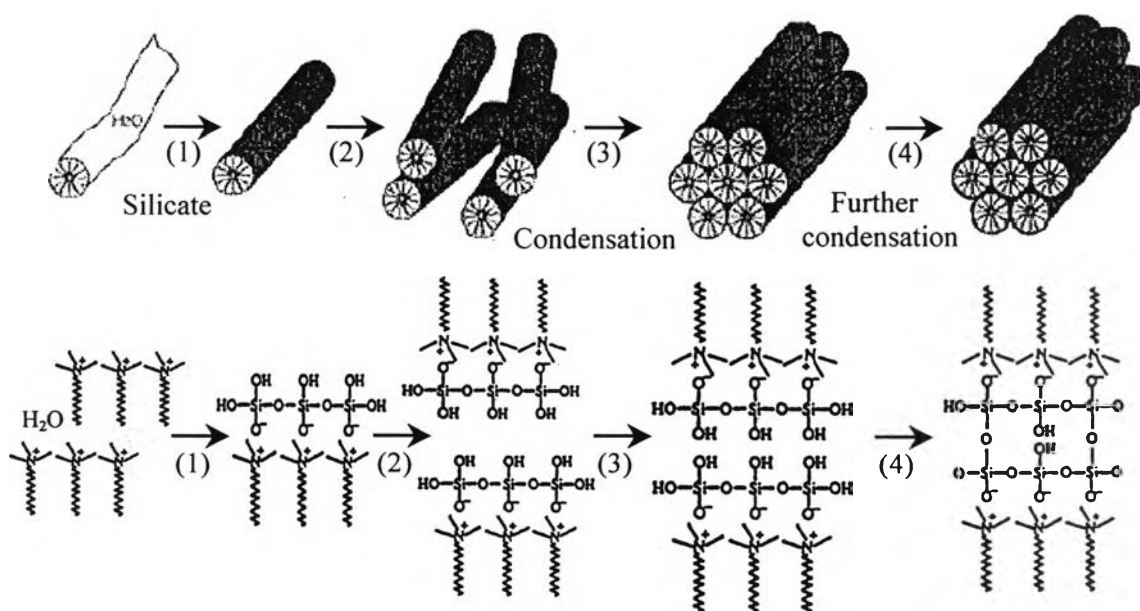


Figure 2.3. Assembly of silicate-encapsulated rods proposed by Davis *et al.* [32]

If one tries to remove the surfactant by calcination, just at the point when the long-range order is achieved, i.e. short synthesis times, the material is not stable as a consequence of the still large number of noncondensed silicate species. Longer synthesis time and/or higher temperature increases the amount of condensed silanols giving as a result stable materials.

Stucky *et al.* [33] developed a model that makes use of the cooperative organization of inorganic and organic molecular species into three dimensionally structured arrays. They divided the global process into three reaction steps. The first step, driven by electrostatic interactions, is the formation of ion pairs between polydentate and polycharged inorganic species on the one hand and the surfactant on the other. The ion pairs then self-organize into a mesophase, having most often a liquid-crystal structure, i.e., hexagonal, lamellar, or cubic. The structure of the mesophase depended on the composition of the mixture, the pH, and the temperature [34]. The last step is the condensation of the inorganic species leading to a rigid structure. Figure 2.4 is a schematic representation of this mechanism.

Following this mechanism, the criteria of charge density matching at the surfactant inorganic interfaces governs the assembly process, and consequently, the final type of structure generated. From this, it can be seen how the principal methodology can be extrapolated to prepare mesophases with different metal oxides as far as there is an electrostatic complementarity among the inorganic ions in solution, the charged surfactant head groups, and, when these charges both have the same sign, inorganic counterions [33]. Four pathways were presented in the synthesis of mesostructured surfactant-inorganic biphasic arrays as shown in Figure 2.5 [34]. In this way, cationic surfactants S^+ are used for the structuring of negatively charged inorganic species I^- (S^+I^- mesostructures). On the other hand, anionic surfactants (S^-) are employed for structuring cationic inorganic species (I^+) (S^-I^+ mesostructures). Organic-inorganic combinations with identically charged partners are also possible, but then the formation of the mesostructure is mediated by the counter-charged ions which must be present in the stoichiometric amounts ($S^+X^-I^+$ and $S^-M^+I^-$ mesostructures). In cases where the degree of condensation of the oligomeric ions which form the walls is low, the removal of the template leads to the collapse of the ordered mesostructure. It would then be of both fundamental and practical interest to develop new synthetic routes which allow the template to be more easily removed.

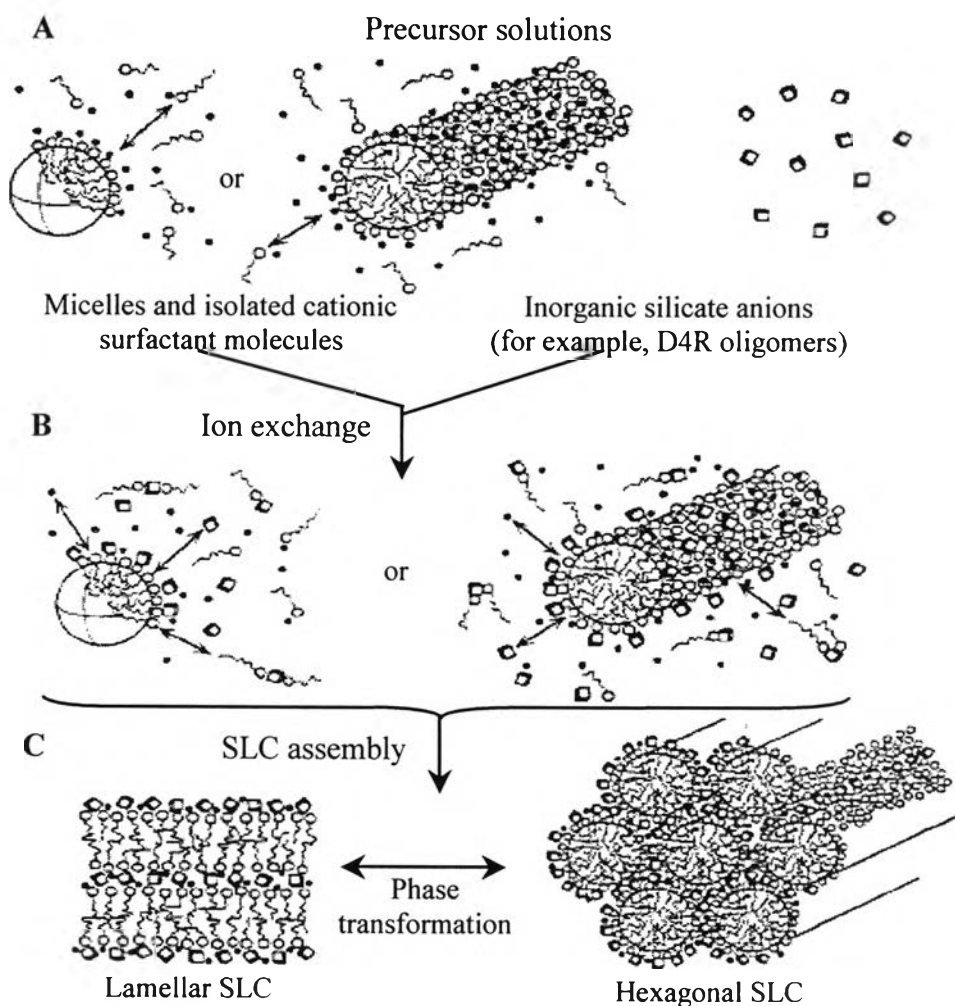


Figure 2.4. Schematic diagram of the cooperative organization of silicate-surfactant mesophases as proposed by Stucky *et al.* [33]

	<i>Surfactant</i>		<i>Inorganic solution species</i>		<i>Examples</i>
Direct pathways	1) Cationic	+	Anionic	S^+I^-	Antimony oxide Tungsten oxide (pH<7) M41S, MCM-48
	2) Anionic	+	Cationic	S^-I^+	Iron oxide Lead oxide Aluminum oxide
Mediated pathways	3) Cationic	+	Cationic	S^+XI^+	Silica (pH<2) Zinc phosphate (pH<3)
	4) Anionic	+	Anionic	S^-MI^-	Zinc oxide (pH>12.5)

Figure 2.5 A general scheme for the self-assembly reaction of different surfactant and inorganic species as proposed by Huo *et al.* [34]

2.4. Sample preparation for metal analysis [35-37]

The determination of metal contained in various samples usually required sample preparation. The major concerning in selection of sample preparation methods for metal analysis are the analytical method to be used, the concentration range of the analyte, and the type of matrix in which the analyte exists. A common result of the sample preparation is the dissolution of the entire sample, producing a clear solution. The digestion method must be selected to suit the type of sample. Dry ashing, wet digestion in acid solution and microwave digestion are common sample preparation methods.

Dry ashing is useful for moist samples such as food or botanical samples because it destroys large amounts of wet organic matters easily and quickly. Dry ashing involves the heating of sample in a silica or porcelain crucible in a muffle furnace in the presence of air at 400-800°C. After decomposition, the residue is dissolved in acid and transferred to a volumetric flask prior to analysis. This allows organic matters to be destroyed. However, the method may also lead to the loss of volatile elements, e.g. Hg, Pb, Cd, As, Sb, Cr and Cu. Thus, compounds such as sodium carbonate or magnesium oxide were added to retard the loss of volatile [38]. Nevertheless, this method has some drawbacks, such as losses due to volatilization, resistance to ashing by some materials, difficult dissolution of ashed materials and high risk of contamination. These drawbacks can be largely overcome using wet digestion.

Wet digestion is usually carried out in an open container. Samples are dried, weighed, and placed in a beaker. The digestion reagent is added. The beaker is covered with a watch glass and placed on a hot plate. The sample is allowed to boil very gently to avoid spattering. More solution may be added from time to time to prevent the sample from drying out. Hydrogen peroxide may be added at a point during the digestion to destroy organic materials. When the sample was completely digested, it is evaporated to near dryness and then take up in a dilute acid solution and diluted to volume for analysis. Samples are generally not allowed to dry completely, as species even less soluble may form. Filtration at this point is often necessary, as many matrices will leave some insoluble matter such as silica. The filtration must be rinsed carefully to avoid the loss of analyte.

Microwave digestion can be carried out in either closed or open vessel, but closed vessels are more popular because of the higher pressures and higher

temperatures that can be achieved. One of the main advantages of microwave decomposition is speed. Typically, microwave decompositions of even difficult samples can be accomplished in 5 to 10 minutes, because microwave energy is transferred directly to all the molecules of solution nearly simultaneously without heating the vessel. Thus, boiling temperature is reached throughout the entire solution very quickly.

2.5. Factorial design

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response [39-40]. Typically, there are several special cases of the general factorial design that are important because they are widely used in research work and also because they form the basis of other designs of considerable practical value.

The importance of these special cases is that of k factors, each at only two levels. These levels may be quantitative such as two values of temperature, pressure or time; or they may be qualitative such as two machines, two operators, the “high” and “low” levels of a factor, or perhaps the presence and absence of a factor. A complete replicate of such a design requires $2 \times 2 \times \dots \times 2 = 2^k$ observations and is called a 2^k factorial design.

The 2^k design is particularly useful in the early stages of experimental work when there are likely to be many factors to be investigated. It provides the smallest number of runs, which k factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments.

The 2^3 design

Suppose that three factors; A, B and C, each at two levels, are of interest. The design is called a 2^3 factorial design and the eight treatment combinations can now be displayed geometrically as a cube, as shown in Figure 2.6. Using the “- and +” notation to represent the low and high levels of the factors, the list of eight runs in the 2^3 design are tabulated in Table 2.1. This is sometimes called the design matrix.

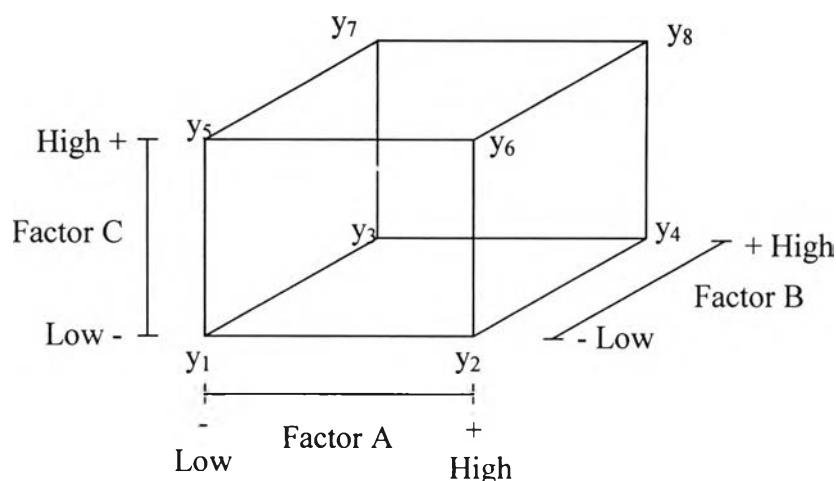


Figure 2.6 Geometric view of the 2^3 factorial design

Table 2.1 Design matrix for 2^3 factorial design

Run	A	B	C	Treatment combination
1	-	-	-	y_1
2	+	-	-	y_2
3	-	+	-	y_3
4	+	+	-	y_4
5	-	-	+	y_5
6	+	-	+	y_6
7	-	+	+	y_7
8	+	+	+	y_8

As shown in Table 2.1, the symbols $y_1, y_2, y_3, y_4, y_5, y_6, y_7, y_8$ represent the total of all n replicates taken at the treatment combination. There are seven degrees of freedom between the eight treatment combinations in the 2^3 design. Three degrees of freedom are associated with the main effects of A, B and C. Four degrees of freedom are associated with interactions; one each with AB, AC, and BC and one with ABC.

The determination of each effect can be calculated from design matrix or columns of contrast coefficient, illustrated in Table 2.2. The contrasts for the main effects are the sign used in the design matrix. These are applied to the response and then divided by 4, since this is the number of comparison mode. Thus, to calculate the A effect:

$$A = \frac{-y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8}{4}$$

The other main effects could be calculated in a similar manner. Note that each effect has four – signs and four + signs associated with it.

For the two-factor interaction, the AB effect is shown below.

$$AB = \frac{+y_1 - y_2 - y_3 + y_4 + y_5 - y_6 - y_7 + y_8}{4}$$

Other two-factor interactions and the three-factor interaction could be obtained in a same manner.

Table 2.2 The columns of contrast coefficients for the 2^3 design

Run	A	B	C	AB	AC	BC	ABC	Response	Variance
1	-	-	-	+	+	+	-	y_1	V_1
2	+	-	-	-	-	+	+	y_2	V_2
3	-	+	-	-	+	-	+	y_3	V_3
4	+	+	-	+	-	-	-	y_4	V_4
5	-	-	+	+	-	-	+	y_5	V_5
6	+	-	+	-	+	-	-	y_6	V_6
7	-	+	+	-	-	+	-	y_7	V_7
8	+	+	+	+	+	+	+	y_8	V_8

If replicated measurements are performed at each of the 2^3 runs in the design, the variance of replication (V) is calculated. Then, the 2^3 variance estimates can be combined to give an overall variance estimate ($\sum V$). Furthermore, the standard error (SE) of the effect is estimated by:

$$SE = \left(\frac{\sum V}{2N} \right)^{1/2}$$

Where V is the variance of replications and N is the number of experiments performed.

The standard error (SE) is used to determine which factor is likely to be important or significant. If the effect value is larger than the standard error, that effect has a significant influence on the tested property.

2.6 Adsorption isotherms [41-43]

An adsorption isotherm describes the relationship between the concentration of adsorbate remaining in solution at equilibrium and its adsorbed extent at constant temperature. A number of isotherm models has been proposed to describe adsorption process but the most common uses are (a) linear sorption isotherm, (b) Langmuir isotherm and (c) Freundlich isotherm (Figure 2.7).

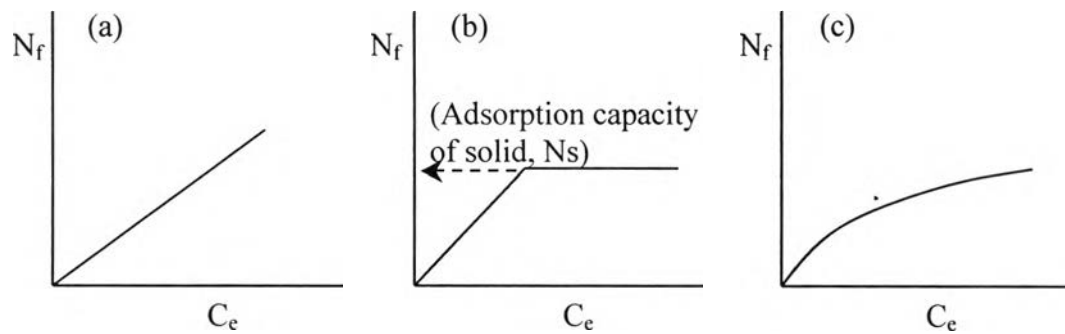


Figure 2.7 The adsorption isotherms: (a) linear sorption isotherm (b) Langmuir isotherm (c) Freundlich isotherm.

If the sorption isotherm is linear, the amount adsorbed, N_f (mg/g) is directly proportional to the concentration of metal at equilibrium, C_e (mg/L) and the slope of the isotherm is referred to the distribution coefficient, K_d . The linear sorption isotherm is expressed as:

$$N_f = K_d C_e \quad (2.9)$$

In the Langmuir model, the adsorption increases linearly with the increasing of solute concentration at low C_e values and approaches a constant value at high concentration. The adsorbed concentration approaches a constant value because there are limited numbers of adsorption sites in solid sorbent. The Langmuir equation can be described mathematically with equation 2.10.

$$N_f = \frac{K_L N_S C_e}{1 + K_L C_e} \quad (2.10)$$

Where, N_f is the amounts of metal adsorbed at equilibrium (mg/g), K_L is the equilibrium constant for the adsorption reaction, N_S is the number of sorption sites (maximum amounts of metal adsorbed) (mg/g) and C_e is the concentration of metal at equilibrium (mg/L). After linearization of the Langmuir isotherm, we obtain:

$$\frac{C_e}{N_f} = \frac{C_e}{N_S} + \frac{1}{K_L N_S} \quad (2.11)$$

The plot of C_e/N_f vs C_e gives a straight line with a slope equal to $1/N_S$ and an intercept equal to $1/K_L N_S$. The values of N_S and K_L are then calculated from the slope and intercept of the Langmuir plot, respectively.

If the number of adsorption sites is large relative to the number of metal ions, it is possible to use the Freundlich isotherm:

$$N_f = K_d C_e^N \quad (2.12)$$

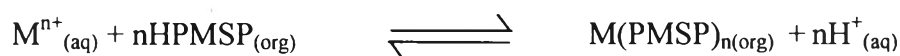
Where N_f is the amounts of metal adsorbed at equilibrium, K_d is the distribution coefficient, C_e is the metal concentration at equilibrium and N is a chemical-specific coefficient. The linear form of Freundlich model derived from equation 2.12 is expressed in the following equation.

$$\log N_f = \log K_d + N \log C_e \quad (2.13)$$

The plot of $\log N_f$ vs $\log C_e$ yields a straight line with a slope equal to N and an intercept equal to $\log K_d$.

2.7. Doping molecule

As described previously, the metal extraction properties of silica could be efficiently promoted by functionalizing this material with a complexing agent. 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP), a kind of β -diketone with the structure shown in Figure 2.8, is an acidic chelating agent that could be served for this purpose. This molecule has a pKa around 4.1 and is well known as a chelating ligand in liquid-liquid extraction. It can form a stable complex with several metal ions such as Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) [12-15, 44]. The reaction between this molecule and metal ions can be expressed as follows.



Where $M(\text{PMSP})_n$ is the metal-chelating agent complex. M^{n+} is the metal ion.

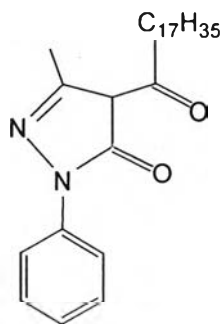


Figure 2.8 Chemical structure of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP)

2.8. Literature review

Recently, the development of new materials for trace metals separation and preconcentration from various samples has been the subject of extensive interest. Several sorbents such as silica, alumina, activated carbon, etc. were created to support this purpose. Among these materials, silica is one of the most popular due to its several advantages including its high versatility, mechanical strength and thermal stability. However, traditional silica is still lack of selectivity. Oftenly, prior to use, the surface of this sorbent is thus needed to be modified in order to work efficiently.

Several researches concerning doping technique, one of the interesting methods of silica functionalization, were reported. Seneviratne and Cox [45] prepared dimethylglyoxime (DMG) doped microporous and mesoporous silica and applied the obtained materials for the extraction of Ni(II). The capacity of DMG-doped mesoporous silica was found to be only 0.009 mol/kg and the leaching of the complexing agent was observed during the extraction experiment. On the contrary, the microporous silica showed no loss of DMG, but the extraction capacity was lowered because of its low permeability.

Khan *et al.* [46] presented a successful route to prepare 1-(2-thiazolylazo)-2-naphthol (TAN) doped silica and applied this sorbent to the removal of Zn(II) from aqueous solution. The maximum adsorption of Zn(II) ions onto the TAN doped sol-gel was found to be 0.035 mol/kg. Also, the desorption of Zn(II) was achieved using 0.1 M HCl as an eluent. The same authors described also the synthesis of 1-(2-pyridylazo)-2-naphthol (PAN) doped silica and the application of this sorbent to the extraction of Cd(II) from aqueous solution [11]. The maximum amount of incorporated PAN was found to be 0.09 mol/kg and the maximum Cd(II) extraction capacity of this sorbent was 0.044 mol/kg. Also, this metal ion could be desorbed by 1 M HCl. The study of adsorption-desorption cycle was repeated four times without the decrease in the sorption efficiency.

For the researches related to the potential pyrazolone ligand, Tong and colleague [15-16] reported the synthesis of HPMSP impregnated microporous silica and the application of this sorbent to the extraction of various metal ions such as Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Mn(II), Zn(II) and Fe(III) from aqueous solution. The conditions for effective adsorption in both batch and column methods were optimized. Several parameters such as pH of metal solution, shaking time and amounts of sorbent were evaluated by batch method, whereas the factors investigated

in column method were the volume of metal solution and flow rate. The experimental results had shown the excellent affinity of this modified sorbent to the extraction of Cu(II) and Fe(III) even at low pH. And the maximum extraction of Co(II), Cu(II) and Ni(II) by this silica was 0.045, 0.043 and 0.049 mol/kg, respectively. The reusability of the sorbent was also performed ten times without considerable loss of adsorption capacity. Furthermore, this modified silica was successfully applied for the preconcentration of metal ions in sodium chloride medium and from tap water.

The functionalization of microporous silica by these HPMSP molecules using the new doping technique was first introduced by Intasiri [17]. Various synthesis parameters, the physical and the Cu(II) extraction properties of materials were investigated. The author concluded that the Cu(II) extractability of the sorbent depended mainly on the surface area of microporous silica. To determine the principal influence parameters on the surface area, three parameters including speed of drying, temperature and gelation time were studied using factorial design as a method. The results had shown that a significant factor was the speed of drying. For the sorption behaviors of this HPMSP doped microporous sorbent, three metal ions such as Co(II), Cu(II) and Ni(II) were studied and the sorption experiments were carried out in both batch and column methods. The results had shown that the extractability of this microporous sorbent to Co(II), Cu(II) and Ni(II) was 0.03, 0.04 and 0.04 mol/kg, respectively. In addition, this modified microporous silica was successfully applied to the preconcentration of trace metal from tap water.

Intasiri *et al.* prepared also the HPMSP doped mesoporous silica for serving as a sorbent [17-18]. The authors concluded that the HPMSP doped mesoporous silica was better than the same functionalized microporous sorbent in terms of facility, rapidity and reproducibility of the synthesis. Furthermore, the Cu(II) sorption capacity of the mesoporous silica was approximately 5 times greater than that of microporous sorbent.

The organic system in this mesoporous silica was later investigated by ^1H HRMAS NMR [47]. From this research, the surfactant molecules in the modified silica could be classified into two types: bound CTAB and free CTAB. The bound CTAB is the templating surfactant which is bonded by electrostatic interaction to the silica surface whereas the free CTAB interacts with the encapsulated HPMSP molecule by electrostatic and hydrophobic interactions to form ion pairs at the same ratio.

Later, the influence of parameters on the synthesis of HPMSP doped mesoporous silica was investigated by the same research group [19]. Two parameters such as concentration of NaOH used as catalyst and amounts of functionalized molecules were investigated. The author concluded that the appropriate concentration of NaOH for the synthesis should be 0.1 M. For the extent of functionalized molecules, the author recommended the number 0.06 as the mole ratio of HPMSP/TEOS used for the synthesis since higher extent of HPMSP would result to the difficulty in dissolution of these molecules. Then, the extraction properties of the HPMSP doped mesoporous silica synthesized with the mole ratio of HPMSP/TEOS equal to 0.06 was examined by batch method. The target metal ions were Co(II), Cu(II) and Ni(II) and the parameters studied were pH of metal solution, initial metal concentration, amounts of silica and the presence of foreign ions in metal solution. The sorbent had shown a high adsorption affinity to the extraction of Cu(II) even at low pH. For the adsorption of Co(II) and Ni(II), the pH of metal solution should be higher than 4 to acquire a maximum uptake. In addition, the sorption capacity of this sorbent was greatly influenced by the presence of foreign ions in metal solution. The study of adsorption rate revealed an excellent kinetic sorption of this modified silica due to its high rate of equilibrium attainment. The desorption efficiency of the silica was also performed and 1 M HNO₃ was proposed as an effective eluting agent.

According to the literature mentioned above, the investigation of metal extraction properties of HPMSP doped mesoporous silica was still limited. Most studies were focused on only some metal ions and normally using the batch method as an extraction procedure. Furthermore, this sorbent has not been yet applied to the extraction of metal from environmental matrices. Therefore, the investigation of adsorption properties of HPMSP doped mesoporous silica towards different metal ions in batch method and the optimization of effective sorption of this sorbent by column process are become the subject of considerable interest. Also, the application of this sorbent to the extraction of metal contained in a real sample is a challenging task.

2.9. Objectives of this study

1. To investigate the influence of parameters on the metal extraction efficiency of HPMSP doped mesoporous silica in both batch and column methods.
2. To demonstrate the potential application of HPMSP doped mesoporous as a sorbent for the extraction of metal contaminated in food samples.