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REVIEW

Current Extraction Methods and Purification Materials for Bioactive Compounds from Natural Plants

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Bioactive compounds are the most important part in natural plants which can be used as herbal medicine and functional food. Extraction of these compounds by different methods and separation of them by solid-phase extraction were discussed in this review. Ionic liquid-based silica, ionic liquid-based polymer, molecular imprinted polymer and monolithic materials have been successfully applied as sorbents to separate the bioactive compounds from natural plants.

Keywords: Bioactive compound, Solid-phase extraction, Ionic liquid-based sorbent, Natural plant.

INTRODUCTION

Herbalism is a traditional medicinal or folk medicine based on the use of natural plants and plant extracts. Natural plant-based remedies are used for both acute and chronic health problems, from treating common colds to controlling blood pressure and cholesterol. Additionally, natural plants are widely used in cosmetic products and as functional food additives[1,2].

One of the emphases of natural plants used as herbs is placed on the active compounds. In order to increase the therapeutic effect of the natural plants, the active compounds should be extracted, concentrated and purified. Water and other organic solvents, such as alcohols and esters, are widely used in extraction step. Liquid-liquid extraction is traditionally used for the separation and purification steps, but the efficiency of this technique is very low. Unnecessary compounds including toxic interference that are mixed with the target compounds in natural plants must be removed through several steps and complex methods.

Therefore, solid-phase extraction (SPE), one of the most convenient and high-performance technology, was developed[3]. It can help minimize the use of organic solvents, which were being regulated as priority pollutants[4]. The selection of sorbent is a key point in solid-phase extraction because it can control the analytical parameters such as selectivity, affinity and capacity[5-7]. For this reason, different kinds of surface modifications were used to modify the surface of classical solid-phase extraction materials (*e.g.*, silica and polymer) to increase the selectivity.

Some new solid-phase extraction sorbents such as ionic liquid-modified silica has successfully been used in separation work because of their characteristic cations and anions[8]. Some reports have examined the application of these particles as sorbent materials to separate some familiar organic compounds[9,10] and to extract active components from natural plants, but the selectivity of these materials was deficiently. In this case, molecular imprinted polymers and monolithic technologies were explored to increase the selectivity. These technologies have greatly potential because of the recognized selectivity for a given compound with easily prepared materials.

Extraction methodologies: Several extraction technologies have been used to extract desired bioactive compounds from natural plants and one of the most traditional and commercial used methods is liquid-solid extraction[11]. Most of the bioactive compounds can be extracted from natural plants but low extraction yield is the disadvantage of this method. Large amount of interference was extracted simultaneously and the target compounds cannot be extracted completely.

Some conventional assisted techniques such as heating, boiling or refluxing were introduced in liquid-solid extraction. However, ionization, hydrolysis and oxidation during the long time extraction were hardly to solve[12,13]. In this case, some other methods with assisted equipments were invited. Ultrasonic-assisted extraction is an important technique for extracting bioactive compounds and this method has been quite adaptable on both small and large scales[14]. The results obtained from Zhang *et al.*[15] and Yang *et al.*[16] researches showed that the ultrasonic-assisted can increase the extraction yields of the bioactive compounds. Also with the increasing of ultrasonic power, the product recoveries were increased[17].

Microwave-assisted extraction is known as an environmental-friendly process with economic advantages than traditional extraction method[18]. The highly localized temperature and pressure can cause selective extraction of bioactive compounds from natural plants at a more rapid rate with higher recoveries[19]. It has been employed in the extraction of bioactive compounds from natural plants. For example, Hu *et al.*[20] and Hayat *et al.*[21] extracted several organic acids from natural plants by this method with a short time and a high recovery. Both ultrasonic assisted extraction and microwave-assisted extraction showed higher efficiency than liquid-solid extraction. However, according to different powers and characteristic of target compounds, the extraction rates of both methods were similar[21,22].

Supercritical fluid extraction (SFE) is considered as another environmental-friendly solvent extraction method in current years. Carbon dioxide, which is non-toxic and non-flammable with low cost and high degree of purity, is the most widely used as supercritical fluid[23]. Because of the low temperature and high pressure of supercritical fluid, it was applied to extract the thermally labile compounds such as oils[23-25]. Also according to different pressure and temperature, other bioactive compounds such as sesquiterpene (β-caryophyllene) and polyphenolic from natural plants can be extracted by super filuid extraction[26,27].

New materials as solid-phase extraction sorbents

Molecular imprinted polymer: Molecular imprinted polymer (MIP) is one of the most famous solid-phase extraction sorbents. Molecular imprinting is a rapidly developing technique for the preparation of polymers having specific molecular-recognition properties[28]. When the template was used in the polymerization process, crosslink and monomer would be polymerized with a special structure and chemical functionality which were the same as the template. After the template was removed, the molecular imprinted polymer had the specific selectivity of bioactive compounds which had similar structure and functional groups as the template (Fig. 1).

According to the ability of selectively of MIP, it was used as the sorbent of solid-phase extraction to remove the interference, selective extract and isolate specific compounds. The application of this method had already been demonstrated with a number of bioactive compounds from natural plants (Table-1).

Ionic liquid-based silica: Ionic liquids contain bulky organic cations (such as N-alkylpyridinium or 1-alkyl-3-methylimidazolium) combined with inorganic or organic anions. Ionic liquids have received a lot of attention in many fields of analytical chemistry[50], such as sample preparation[51], organic synthesis[52-55], liquid-phase extraction[56,57], and chromatographic separations[58], because they are high-tech, green reaction media with excellent chemical properties[59,60].

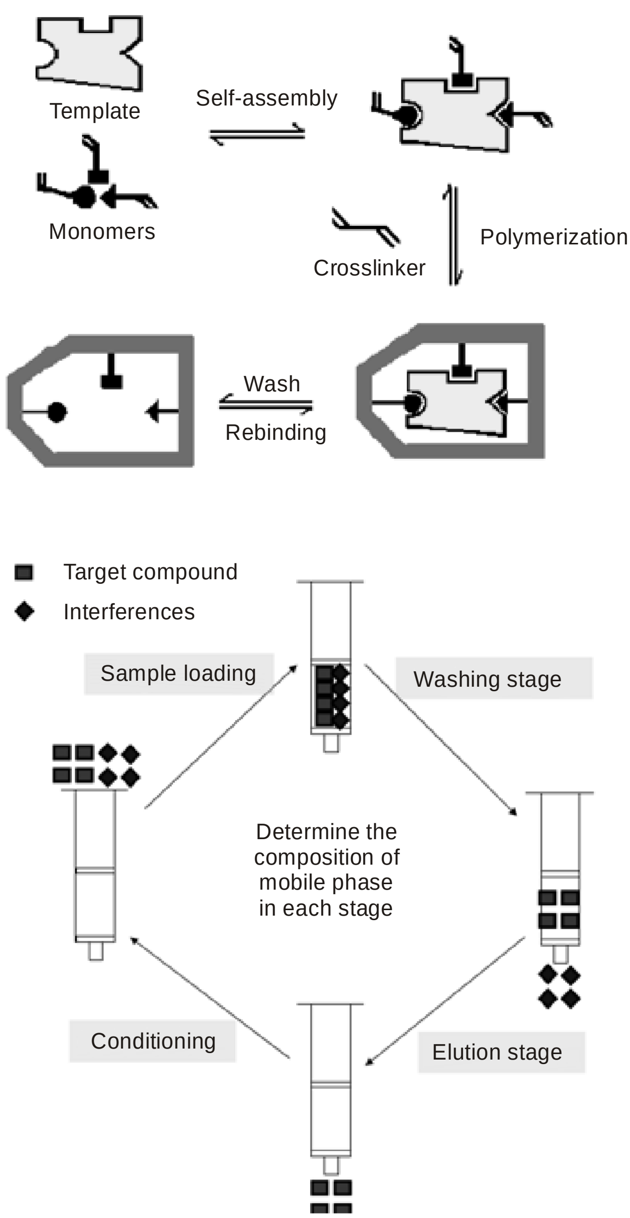

Fig. 1. Principle of MIP-SPE technology

TABLE-1
DIFFERENT CHARACTERISTIC BETWEEN POLYMER AND SILICA AS THE SORBENTS

Characteristic	Substrate	
	Polymer	Silica
Polarity	According to the functional groups	Non-polar
Toxic	Toxic monomer	Non-toxic
Mechanical strength	Low	High
Surface area	Low surface area	Smaller particle size with larger surface area
Functional groups	The type and amount of functional groups can be changed frequently	Large amount of hydroxyl groups
Surface coverage	Because of various functional groups, ionic liquid groups can link with polymer directly	The ionic liquid groups need to synthesize with the hydroxyl groups by silylating agent
Adsorption ability	Particle size of polymer can be adjusted according to the target compounds	Some large size molecular cannot be adsorbed on silica

Zhou *et al*.[61] used weak cation-exchange solid-phase extraction to detect bencycloquidium bromide in human urine. Additionally, Cunliffe *et al*.[62] used this technique to quantify posaconazole in human plasma. Therefore, the anion/cation groups on the surface of sorbent are important. However, these groups have several disadvantages and limitations, such as being toxic and only exhibiting a high efficiency with inorganic ions.

In this case, ionic liquids-based silica was used in separation work because of its characteristic cations and anions. Bi *et al*.[63] used three imidazolium ionic liquid-based silicas as the stationary phases in HPLC columns to separate alkaloids from green tea. The resolutions of the three alkaloids increased with the number of carbon bonds increasing in imidazolium groups (cation groups).

Additionally, ionic liquid-based silicas have been developed as solid-phase extraction sorbents. The surface of the silica can be modified through two methods. Physically grafting method was the one that Li *et al*.[64] already applied to prepare a sorbent which was used to separate α-tocopherol from soybean oil [Fig. 2(A)]. The extraction selectivity for α-tocopherol greatly increased after the sorbent was modified with the ionic liquid. The other method is chemical synthesis modification. Tian *et al*.[65] synthesized an ionic liquid with imidazolium groups on 3-chloro- phropyltrimethoxysilane and then modified the surface of the silica [Fig. 2(B)]. Three tanshinones were separated from the natural plant *Salvia Miltiorrhiza Bunge* using solid-phase extraction cartridges. In addition, two compounds, liquiritin and glycyrrhizic acid, were separated from licorice using another different ionic liquid-based silica sorbent[66]. All of these results revealed that the ionic liquid-based sorbent exhibited a higher selectivity of the target compounds with less interference.

Ionic liquid-modified polymer: Table-2 shows the different characteristics of silica and polymer as the substrate. When silica was used as the substrate, only hydroxyl groups on the surface were involved in the reaction, so the surface coverage was low[67]. When polymer was used, large amounts of available functional groups can be reacted with ionic liquid groups and additional structural selectivity was provided[68,69].

TABLE-2
SUMMARY OF MIP-SPE APPLICATIONS IN NATURAL PLANT

Bioactive compound	Sample	Reagents			Extraction method		
		Template	Monomer	Solvent	Washing solvent	Elution solvent	Ref.
Huperzine A	*Huperzia serrata*	Huperzine A	Acrylamide	Chloroform	Chloroform	Methanol/ ammonia water	29
Sinomenine	*Sinomenium acutum Reht. et Wils*	Sinomenine	MAA[1]	Dodecanol	Methanol	Methanol/AA[2]	30
α-Tocopherol	Bay leaves	α-Tocopherol	MAA[1]	Chloroform	Ethanol/water	Ethanol/AA	31
(-)-Ephedrine	Chinese Ephedra	(-)-Ephedrine	MAA[1]	ACN[3]	ACN	Methanol/TFA[4]	32
Catechol	Tea	Catechol	4-VPy[5]	ACN[3]	ACN	ACN/ nitric acid	33
p-Hydroxy-benoic acid	*Melissa officinalis*	Protocatechuic acid	Acrylamide	ACN[3]	Water/ACN	Methanol/acetic acid	34
Triterpene acid	*Glycirrhiza Glabra*	18-β-Glycyrrhetinic acid	MAA[1]	Chloroform	Chloroform	Methanol	35
Polyphenols	Olive mill waste waters	Caffeic acid, *p*-hydroxybenzoic acid	4-VPy, Allylurea, MAA, Allylaniline	Tetrahydrofuran	Water	Methanol/AA	36
Quercetin	*Cacumen platycladi*	Quercetin	Acrylamide	Tetrahydrofuran	Water	Methanol/AA	37
Matrine	*Sophora flavescens Ait*	Matrine	MAA[1]	Chloroform	Methanol	Methanol/AA	38
Fumonisin B	Yellow bell pepper	Fumonisin B	DEAEM[6]	ACN[3]	Acetone /ethylacetate	Methanol/ chloroform/AA	39
Glabridin	Licorice root	Glabridin	Hydroxyethyl methacrylate	Ethanol-dodecanol	Methanol/water	ACN/TFA	40
Esculetin, esculin, coumarin, *et al*.	Ash bark	Esculetin	Acrylamide	Ethanol	Ethanol/water	DMF[7]/ethanol/water	41
L-Theanine	Green Tea	L-Theanine	Nylon-6	Formic acid	Water	Water/AA, methanol/AA	42
Epicatechin	Tea beverage	Epicatechin	Acrylamide	acetone	Methanol/water	Methanol/AA	43
(+)-Catechin	Green Tea	(+)-Catechin	Acrylamide	ACN[3]	Water/ACN	Methanol	44
17β-Estradiol	Milk powder	17β-Estradiol	TFMAA[8]	ACN[3]	ACN/water	ACN	45
Caffeine	Food sample	Caffeine	MAA[1]	ACN or chloroform	Sodium phosphate buffer	Methanol/AA	46
17β-Estradiol	Water	β-Estradiol	MAA[1]	ACN or ACN/water	ACN	Methanol/AA	47
Quercetin, rutin	Wines, orange juice, tea	Quercetin	4-Vpy[5], MAA[1]	DMSO[9], ACN, DMF	Ethanol/water	Methanol	48
Ursolic acid, oleanolic acid	Ilex kudingcha C.J. Tseng	Ursolic acid	EDMA[10]	DMF	Ethanol/water	Ethanol/water	49

[1]Methacrylic acid. [2]Acetic acid. [3]Acetonitrile. [4]Trifluoroacetic acid. [5]4-Vinylpyridine. [6]2-(diethylamino) ethyl methacrylate. [7]N,N-Dimethylformamide. [8]2-(Trifluoromethyl) acrylic acid. [9]Dimethyl sulfoxide. [10]Ethyl glycol dimethacrylate

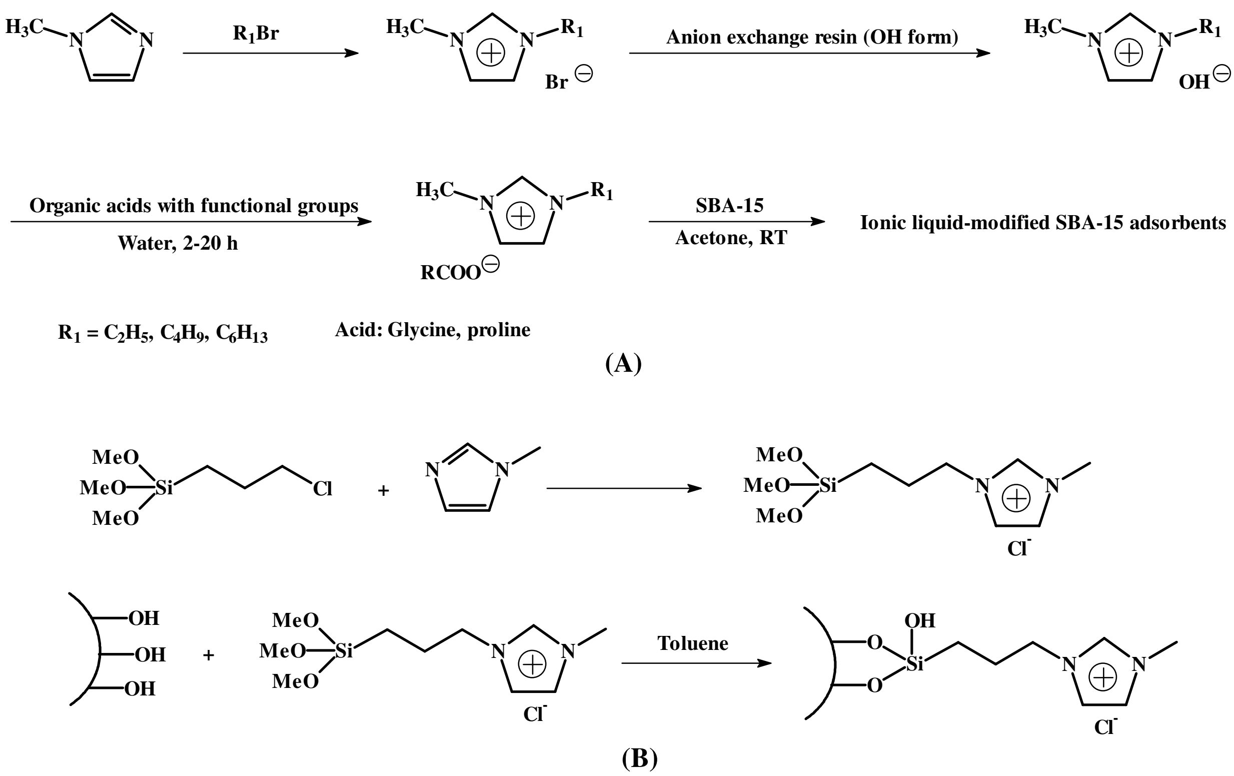

Fig. 2. Ionic liquid-modified surface of silica. (A) physically grafting method, (B) chemical reaction

The results in previous researches revealed that the ionic liquid groups increased the separation efficiency of polymer as the stationary phase. Therefore, the ionic liquid-modified polymer was applied in the solid-phase extraction process. A new polymer that was modified with the IL-CF_3COO- group was used to separate the pharmaceuticals from the aqueous samples[70]. The ionic liquid-modified polymer was capable of selectively and quantitatively extracting a group of acidic compounds. Furthermore, the extraction of caffeine and theophylline from green tea was conducted[71]. The target compounds were separated using different solvents because of the different interactions among ionic liquid groups, caffeine and theophylline along with the interference.

Monolithic and ionic liquid-modified monolithic sorbents: Monoliths consist of single piece of highly porous organic or inorganic material with pores made up of highly interconnected channel network resulting in high effective porosity and thus enabling efficient flow of the mobile phase[72,73]. Organic polymeric monolithic material has benefits of good permeability, a fast mass transfer property, a strong enrichment capability, high stability and ease of modification, which can be widely used as the stationary phase or sorbent in solid-phase extraction[74]. Körner and Kohn[75] used reversed-phase monolithic column to separate the colchicine and related degradation products from natural plant *Colchicum autumnale* L. Then, monolithic column was applied in solid-phase extraction to separate caffeine and theophylline[76]. The results show that the monolithic solid-phase extraction high sensitivity and appropriate precision can be used to separate the bioactive compounds.

According to the research from Wei *et al.*,[77] the ion-exchange was one of mechanisms of solid-phase extraction monolithic column. In order to increase the effect of ion-exchange functional groups, ionic liquids were used to modify the functional groups.

Application of solid-phase extraction on marine plants: The majority of the natural plants that were used in previous literature were from land. In recent decades, marine plants, which grow in the sea water that covers 70.8 % surface of the earth, have attracted a great deal of attention because of the decreasing amount of natural plant resources on land. Therefore, extraction of bioactive compounds from marine plants was applied and solid-phase extraction technology was invited.

Algae are one of the major marine plants or seaweeds. They are a large and diverse group of simple and typically organism which contain lots of bioactive compounds. In Table-3, several bioactive compounds were extracted from different algae with or without solid-phase extraction. They concluded that the extraction procedures and solid-phase extraction method can be useful for the rapid extraction of bioactive phenols from algae materials.

Conclusion

Solid-phase extraction is a powerful analytical tool, which is capable of solving many problems that occur in the separation of bioactive compounds from natural plants because of the high selectivity ability of the sorbents. The characteristics of the ionic liquid-based silica and polymer such as ion-exchange and hydrophilic/hydrophobic characters can be modified frequently according to the functional groups of ionic liquid. The application of molecular imprinted polymer as sorbents not only allowed the pre-concentration and cleanup of the samples but also the selective extraction of the target analytes, which were important, particularly when the samples

TABLE-3
EXTRACTION OF BIOACTIVE COMPOUNDS FROM MARINE PLANTS

Target compounds	Sample	Extraction method	Solid phase extraction	Ref.
Volatile metabolites and essential oils	Brown alga: *Dictyopteris membranacea*	HD[1], FMAHD[2] and SFE[3]	–	78
Sterols	4 Brown algaes	Liquid-solid extraction: methanol/chloroform (50:50)	–	79
Okadaic acid	Algae	Liquid-solid extraction: methanol/water (80:20)	SPE with polyclonal antibodies immobilized silica as the sorbent	80
Sterols	Red alga: *Asparagopsis armata*	Liquid-solid extraction: methanol/chloroform (50:50)	SPE with C_{18} as the sorbent	81
Microcystins	Blue-green algae: *Microcystis aeruginosa*	Liquid-solid extraction: methanol/water (75:25)	SPE with Sepharose® and silica as the sorbents	82
Triacylglycerols and free fatty acids	8 Species of algae	Ternary solvent extraction: dichloromethane (20 %) in *n*-hexane	SPE utilizing sodium carbonate as the sorbent	83
Microcystins	*Chlorella* and *Spirulina*	Methanol or 5 % acetic acid	SPE with C_{18} and silica as the sorbent	84

[1]Hydrodistillation. [2]Focused microwave-assisted hydrodistillation. [3]Supercritical fluid extraction

were complex and impurities interfered with the quantification. Monolithic materials provide both well-documented advantages and limitations. It was improved separations in HPLC and selected as the right phases for isolation of specific analytes for solid-phase extraction.

However, solid-phase extraction sorbents still need to be improved for separation. First, surface coverage of ionic liquid-based materials need to be increased to improve the selectively of target compounds. Secondly, in order to scale-up the synthesized sorbents, the toxicity (from the monomer of polymer or from the functional groups) of the sorbents should be decreased. Thus, more researches on solid-phase extraction for natural plants and marine plants must be conducted in the future.

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