EXTRACTION AND SEPARATION OF PARABENS IN AQUEOUS BIPHASIC SYSTEMS

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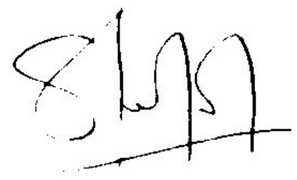
Candidate's Signature  Date 5/5/2014

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Abstract

In this study, five systems for extraction of parabens were developed, namely ionic liquid based aqueous two-phase system (IL-ATPS), ionic liquid based aqueous two-phase system with β-cyclodextrin (IL-βCD-ATPS), cloud point extraction (CPE-DC193C), cloud point extraction with β-cyclodextrin (CPE-DC193C-βCD) and cloud point extraction with β-cyclodextrin-ionic liquid (CPE-DC193C-βCD-IL). These five developed methods have been optimized in order to get the optimum conditions for phase separation of parabens in water samples. These new, green, fast and simple extraction techniques coupled with a reversed-phase high performance liquid chromatography (RP-HPLC) showed excellent results for extracting parabens from aqueous samples. β-CD and βCD-IL as modifiers improved the sensitivity of IL-ATPS and CPE-DC193C systems. The experimental results demonstrated that the method detection limits (LOD) for studied parabens using IL-βCD-ATPS were in the range of 0.022-0.075 μgmL^{-1} and CPE-DC193C-βCD-IL methods were in the range of 0.013-0.038 μgmL^{-1}. These LOD results were relatively lower compared with IL-ATPS, CPE-DC193C and CPE-DC193C-βCD methods. Addition of β-CD and βCD-IL as modifiers also improved the selectivity of the developed methods. The use of IL-βCD-ATPS reduced the matrix effect and hence, percentage of recovery of parabens extraction increased from 88.0-92.8% to 96.0-98.5%. The recoveries of parabens extraction in sea water using IL-ATPS were dramatically improved with addition of β-CD in the IL-βCD-ATPS method. The mixture of βCD-IL with the surfactant molecules and parabens in the formation of micelles produced the extra large complex formations during the CPE process. The CPE-DC193C-βCD-IL system offered an obviously lower phase volume ratio compared to CPE-DC193C-βCD and CPE-DC193C systems with the value of phase volume ratios as 0.74, 0.92 and 1.63 respectively at 30% (w/v) surfactant concentration. On the other hand, IL-βCD-ATPS system also showed a lower phase volume ratio with the value of 0.16 compared to 0.19 for IL-ATPS at 30% (w/v) ionic liquid concentration. The developed method of CPE-DC193C-βCD-IL showed the highest preconcentration factor with the values for MeP (methyl paraben), EtP (ethyl paraben), PrP (propyl paraben) and ArP (benzyl paraben) were 76, 89, 97 and 110, respectively. While, the highest preconcentration factors for IL-βCD-ATPS were 70, 86, 95 and 103 for MeP, EtP, PrP and ArP respectively. When the surfactant concentration was increased from 5% (w/v) to 60% (w/v), ArP in CPE-DC193C-βCD-IL method the measured total loss of water content was 68%. ArP lost about 50 % (w/v) water content

in IL-βCD-ATPS compared to IL-ATPS where ArP lost only 43 % (w/v) water content when the ionic liquid concentration increased. It shows that CPE-DC193C-βCD-IL is considered as the highest loss of water content compared to the CPE-DC193C-βCD, CPE-DC193C, IL-βCD-ATPS and IL-ATPS systems. The overall loss of water content for MeP was 55%, followed by EtP and PrP with 52% each in CPE-DC193C-βCD-IL. Moreover, the distribution coefficient of parabens in surfactant-rich and ionic liquid rich phase in the order of hydrophobicity of parabens is MeP<Etp<PrP<ArP. In conclusion, βCD-IL contributes to a higher distribution of parabens in surfactant-rich phase compared to the other methods.

Abstrak

Kajian ini membangunkan lima sistem pengekstrakan paraben iaitu pengekstrakan cecair ionik berasaskan sistem akueus dua fasa (IL-ATPS), cecair ionik berasaskan sistem akueus dua fasa dengan β-siklodektrin (IL-βCD-ATPS), pengekstrakan titik awan (CPE-DC193C), pengekstrakan titik awan dengan β-siklodektrin (CPE-DC193C-βCD) dan pengekstrakan titik awan dengan cecair β-siklodektrin-ionik (CPE-DC193C-βCD-IL). Sistem-sistem ini diaplikasikan bagi mendapatkan keadaan optimum untuk pemisahan fasa paraben dari sampel air. Sistem-sistem ini adalah teknik pengekstrakan yang baru, hijau, cepat, mudah dan digabungkan dengan kromatografi cecair prestasi tinggi fasa-berbalik (RP-HPLC) telah menunjukkan keputusan cemerlang untuk mengeluarkan parabens dari sampel air. β-CD dan βCD-IL sebagai ejen pengubah meningkatkan kepekaan sistem IL-ATPS dan CPE-DC193C. Keputusan eksperimen menunjukkan bahawa had pengesanan (LOD) untuk paraben yang dikaji menggunakan kaedah IL-βCD-ATPS berada dalam julat 0.022-0.075μgmL^{-1} manakala kaedah CPE-DC193C-βCD-IL berada dalam julat 0.013-0.038 μgmL^{-1}. Nilai LOD ini ialah lebih rendah dibandingkan dengan kaedah IL-ATPS, CPE-DC193C dan CPE-DC193C-βCD. Penambahan β-CD and βCD-IL sebagai ejen pengubah juga meningkat kepilihan kaedah yang dibangunkan. Penggunaan IL-βCD-ATPS mengurangkan kesan matriks, seterusnya peratusan pemulihan pengekstrakan paraben bertambah dari 88.0-92.8% hingga 96.0-98.5%. Kebolehdapatan pengekstrakan paraben dari air laut menggunakan IL-ATPS meningkat dengan dramatik dengan penambahan β-CD dalam kaedah IL-βCD-ATPS. Campuran βCD-IL dengan molekul surfaktan dan paraben dalam pembentukan misel menghasilkan formasi kompleks ekstra besar semasa proses CPE. Sistem CPE-DC193C-βCD-IL menawarkan nisbah isipadu fasa yang jauh lebih rendah berbanding sistem CPE-DC193C-βCD and CPE DC193C dengan masing-masing bernilai 0.74, 0.92 dan 1.63 pada kepekatan surfaktan 30% (w/v). Manakala sistem IL-βCD-ATPS juga menunjukkan nisbah isipadu fasa lebih rendah dengan nilai 0.16 berbanding dengan 0.19 untuk IL-ATPS pada kepekatan cecair ionik 30% (w/v). Kaedah CPE-DC193C-βCD-IL yang dibangunkan menunjukkan faktor pra-kepekatan tertinggi dengan nilai untuk metil paraben (MeP), etil paraben (EtP), propil paraben (PrP) dan benzil paraben (ArP) masing-masing ialah 76, 89, 97 dan 110. Manakala, faktor pra-kepekatan tertinggi untuk IL-βCD-ATPS ialah 70, 86, 95 dan 103 masing-masing untuk MeP, EtP, PrP and ArP. Apabila kepekatan surfaktan ditingkatkan dari 5% hingga 60% dalam kaedah CPE-DC193C-βCD-IL jumlah kehilangan kandungan air

adalah 68%. ArP kehilangan air sebanyak 50% (w/v) dalam kaedah IL-βCD-ATPS berbanding dengan kaedah IL-ATPS yang kehilangan air sebanyak 43% (w/v) sahaja apabila kepekatan cecair ionik meningkat. Peratusan ini adalah kehilangan kandungan air tertinggi berbanding dengan sistem CPE-DC193C-βCD and CPE-DC193C. Kehilangan kandungan kandungan air secara keseluruhannya adalah 55% untuk MeP, diikuti oleh EtP and PrP masing-masing dengan 52%. Pekali taburan paraben dalam cecair yang kaya dengan surfaktan dan cecair ionik fasa mengikut susunan kehidrofobisiti paraben ialah MeP<EtP<PrP<ArP. Secara kesimpulannya, βCD-IL menyumbang kepada pengagihan paraben lebih tinggi di fasa yang kaya dengan surfaktan berbanding dengan kaedah-kaedah yang lain.