# ABSTRACT

β-Cyclodextrin functionalized ionic liquid polymer (βCD-BIMOTs-TDI) was first synthesized by functionalized β-cyclodextrin (CD) with 1-benzylimidazole (BIM) to form monofunctionalized CD (βCD-BIMOTs), and was further polymerized using toluene diisocyanate (TDI) as a linker to form insoluble βCD-BIMOTs-TDI. The βCD-BIMOTs-TDI was characterized using various tools and the results obtained were compared with those derived from the native β-cyclodextrin polymer (βCD-TDI). The scanning electron microscope (SEM) results showed that the presence of ionic liquid (IL) increased the pore size, while the thermo gravimetric analysis (TGA) results showed that the presence of IL increased the stability of the βCD-BIMOTs-TDI. Meanwhile, Brunauer-Emmett-Teller (BET) result showed that βCD-BIMOTs-TDI had 1.254 $m^2/g$ surface area, and the Barret-Joyner-Halenda (BJH) pore size distribution result revealed that the polymer exhibited macropores with a pore size of 77.66 nm. Preliminary sorption experiments were carried out and the βCD-BIMOTs-TDI polymer showed enhanced sorption capacity and high removal towards phenols. Based on preliminary sorption experiment, 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 2,4-dinitrophenol (2,4-DNP) were selected for batch adsorption study. The removal was found to be pH dependent, and therefore, pH 6 was selected for the adsorption process of 2,4-DCP and 2,4,6-TCP since optimum removal was observed at this range. In comparison, pH 4 was selected for the adsorption of 2,4-DNP. A kinetic analysis showed that the pseudo-second-order equation provided better fit for the adsorption of the studied phenols (correlation coefficient ($R^2$) values ranged from 0.9996-1) with 120 min as the equilibrium time. The adsorption process on βCD-BIMOTs-TDI was found to be in the order of 2,4-DNP > 2,4,6-TCP > 2,4-DCP. Meanwhile, external and intraparticle diffusion simultaneously occurred during the

adsorption process of 2,4-DCP, 2,4,6-TCP, and 2,4-DNP onto βCD-BIMOTs-TDI, but it was not a rate determining step. As for the study of isotherm, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich's models were studied, and Freundlich's isotherm was found to fit well for the adsorption of 2,4-DCP, and 2,4,6-TCP with $R^2$>0.97 for all studied temperatures. On the other hand, Langmuir's model was found to fit well with the adsorption of 2,4-DNP on βCD-BIMOTs-TDI. Besides, the thermodynamics results showed that the adsorption process of 2,4-DCP was exothermic since a negative value of ΔH° (-18.10) was obtained, while the positive values of ΔH° (40.27, and 2.38) indicated that the adsorption process of 2,4,6-TCP, and 2,4-DNP had been endothermic. In addition, adsorption mechanism was studied and was proposed by considering inclusion complex and π-π interaction between modified β-CD functionalized IL (βCD-BIMOTs) with one selected phenol compound (2,4-DCP). Apart from that, a new method was developed by applying βCD-BIMOTs-TDI as an adsorbent material for solid phase extraction (SPE) of phenols in water samples by using Gas Chromatography–Flame Ionization Detector (GC-FID). Six different types of phenols; 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), 4-chloro-3-methylphenol (4-CMP), and 2,4,6-Trichlorophenol (2,4,6-TCP) as model analytes, were extracted on a βCD-BIMOTs-TDI SPE cartridge. The optimum experimental condition was 15 mL of sample volume (sample at pH 6), and 2 mL of methanol containing 1% acetic acid as an eluent solvent. The developed method (βCD-BIMOTs-TDI-SPE) was then compared with other adsorbents and the obtained results showed that the βCD-BIMOTs-TDI exhibited higher extraction recovery due to the unique structure and properties. High sensitivity (detection limits 0.23-0.35 µg/L) and good recoveries (87%-116%) were achieved with satisfactory relative standard deviation (RSDs) (0.1-1.7%). Finally, under optimized condition,

βCD-BIMOTs-TDI was applied as an SPE sorbent for determination of phenols in river and tap waters, prior to GC-FID separation.

# ABSTRAK

β-Cyclodextrin berfungsikan cecair ionik polimer (βCD-BIMOTs-TDI) pertama kali disintesis oleh β-cyclodextrin (CD) berfungsi dengan 1-benzylimidazole (BIM) untuk membentuk monoberfungsi CD (βCD-BIMOTs), dan seterusnya dipolimerkan dengan menggunakan diisosianat toluena (TDI) untuk membentuk polimer yang tidak larut, iaitu βCD-BIMOTs-TDI. βCD-BIMOTs-TDI dicirikan dengan menggunakan pelbagai alat dan keputusan yang diperolehi dibandingkan dengan β−siklodekstrin polimer (βCD-TDI). Hasil keputusan pengimbasan elektron mikroskop (SEM) menunjukkan bahawa kehadiran cecair ionik (IL) meningkatkan saiz liang, sementara keputusan analisis thermogravimetrik (TGA) menunjukkan bahawa kehadiran IL meningkatkan kestabilan βCD-BIMOTs-TDI. Sementara itu, keputusan Brunauer-Emmett-Teller (BET) menunjukkan bahawa βCD-BIMOTs-TDI mempunyai luas permukaan 1.254 $m^2/g$, dan keputusan taburan saiz liang Barret-Joyner-Halenda (BJH) mendedahkan bahawa polimer mempamerkan liang makro dengan saiz liang 77.66 nm. Ujikaji penyerapan awal telah dijalankan dan polimer βCD-BIMOTs-TDI menunjukkan kapasiti penyerapan dipertingkatkan dan penyingkiran yang tinggi terhadap sebatian fenol. Berdasarkan eksperimen penyerapan awal, 2,4-dichlorophenol (2,4-DCP), 2,4,6-triklorofenol (2,4,6-TCP), dan 2,4-dinitrophenol (2,4-DNP) telah dipilih untuk kumpulan kajian penjerapan. Penyingkiran didapati bergantung terhadap pH dan oleh itu, pH 6 telah dipilih untuk proses penjerapan 2,4-DCP dan 2,4,6-TCP disebabkan penyingkiran optimum diperhatikan pada julat ini. Sebagai perbandingan, pH 4 dipilih bagi penjerapan 2,4-DNP. Analisis kinetik menunjukkan bahawa persamaan pseudo-tertib kedua menyediakan penjerapan yang lebih sesuai bagi fenol yang dikaji (nilai $R^2$ yang terdiri 0.9996-1) dengan masa keseimbangan 120 min. Proses penjerapan pada βCD-BIMOTs-TDI didapati dalam turutan 2,4-DNP > 2,4,6-TCP > 2,4-DCP .

Sementara itu, lapisan dan difusi intrapartikal berlaku serentak semasa proses penjerapan 2,4-DCP, 2,4,6-TCP dan 2,4-DNP ke βCD-BIMOTs-TDI tetapi ia bukan langkah kadar penentu. Untuk kajian isoterma, model-model Langmuir, Freundlich, Temkin, dan Dubinin-Radushkevich dikaji dan isoterma model Freundlich didapati sangat sesuai bagi penjerapan 2,4-DCP dan 2,4,6-TCP dengan $R^2 > 0.97$ untuk semua suhu yang dikaji. Sebaliknya, model Langmuir didapati sangat sesuai dengan penjerapan 2,4-DNP pada βCD-BIMOTs-TDI. Keputusan termodinamik menunjukkan bahawa proses penjerapan 2,4-DCP adalah eksotermik disebabkan nilai ΔH° (-18.10) adalah negative, sementara nilai positif ΔH° (40.27, 2.38) menunjukkan bahawa proses penjerapan 2,4,6-TCP dan 2,4-DNP adalah endotermik. Mekanisme penjerapan telah dikaji dan dicadangkan dengan mempertimbangkan kompleks kemasukan dan interaksi π-π antara β-CD berfungsi IL (βCD-BIMOTs) dengan satu sebatian fenol yang dipilih (2,4-DCP). Selain itu, kaedah baru telah dibangunkan dengan menggunakan βCD-BIMOTs-TDI sebagai bahan penjerap untuk pengekstrakan fasa pepejal (SPE) untuk fenol di dalam sampel air dengan menggunakan kromatografi gas-pengesan nyalaan Pengionan (GC-FID). Enam jenis fenol, iaitu 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), 4-chloro-3-methylphenol (4-CMP), dan 2,4,6-Trichlorophenol (2,4,6-TCP) sebagai model analit, telah diekstrak pada βCD-BIMOTs-TDI kartrij SPE. Keadaan eksperimen optimum adalah 15 mL isipadu sampel (sampel pada pH 6) dan 2ml metanol yang mengandungi 1 % asid asetik sebagai pelarut larutan. βCD-BIMOTs-TDI-SPE yang dibangunkan kemudian dibandingkan dengan penjerap yang lain dan keputusan yang diperolehi menunjukkan bahawa βCD-BIMOTs-TDI mempamerkan pemulihan pengekstrakan yang lebih tinggi disebabkan oleh struktur dan ciri-ciri unik. Sensitiviti yang tinggi (had pengesanan 0,23-0,35 μg / L) dan pemulihan yang baik (87% -116%) telah dicapai dengan memuaskan sisihan piawai relatif (RSDs) (0,1-1,7%). Akhirnya, di bawah keadaan optimum, βCD-

BIMOTs-TDI telah digunakan sebagai penjerap bagi pengekstrakan pepejal untuk penentuan fenol dalam air sungai dan air paip, sebelum menggunakan pemisahan GC-FID.

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| CDs | Cyclodextrins |
| CD | Cyclodextrin |
| IL | Ionic Liquid |
| $^{o}C$ | Degree Celsius |
| $cm^3$ | Centimetre cube |
| $dm^3$ | Decimetre cube |
| $TS_2O$ | p-toluene sulfonic anhydride |
| β-CDOTs | 6-O-Monotosyl-6-deoxy-β-cyclodextrin |
| βCD-BIMOTs | Mono-6-deoxy-6-(3-benzylimidazolium)-β-cyclodextrin |
| βCD-BIMOTs-TDI | β-cylodextrin functionalized ionic liquid polymer |
| βCD-TDI | β-cyclodextrin polymer |
| µg/L | Parts per billion |
| mg/L | Parts per million |
| k | Kilo |
| K | Kelvin |
| J | Joule |
| m | Metre |
| g | Gram |
| min | Minute |
| cm | Centimetre |
| L | Litre |
| mol | Mole |
| % | Percentage |