

SINTESIS SERI C-ALKOKSIFENILKALIKS[4]RESORSINARENA TRIFENILFOSFONIUM KLORIDA SERTA PENGGUNAANNYA SEBAGAI ADSORBEN Cr(VI), REMAZOL BRILLIANT BLUE R (RBBR), DAN SODIUM DODECYLBENZENE SULFONATE (DBS)

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INTISARI

Telah dilakukan sintesis senyawa kaliks[4]resorsinarena baru bermuatan positif seri C-alkoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida. Sintesis dilakukan dari vanilin (4-hidroksi-3-metoksibenzaldehida) melalui reaksi alkilasi, substitusi elektrofilik aromatik dan siklisasi, klorometilasi, dan reaksi substitusi nukleofilik bimolekuler. Elusidasi struktur produk dilakukan menggunakan spektrofotometer FTIR dan NMR, SEM dan BET. Senyawa kaliks[4]resorsinarena bermuatan positif, C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida dan C-3,4-dimetoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida selanjutnya digunakan sebagai adsorben kromium heksavalen (Cr(VI)), *Remazol Brilliant Blue R* (RBBR), dan *Sodium Dodecylbenzene Sulfonate* (DBS). Parameter adsorpsi yang digunakan yaitu pH, kinetika, dan isoterm adsorpsi.

Reaksi 4-hidroksi-3-metoksibenzaldehida dengan dietil sulfat terkatalisis NaOH direfluks selama 4 jam dan menghasilkan 4-etoksi-3-metoksibenzaldehida sebanyak 99,16%. Substitusi elektrofilik aromatik dan siklisasi produk etilasi dan metilasi dengan resorsinol dan HCl menghasilkan C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena dan C-3,4-dimetoksifenilkaliks[4]resorsinarena masing-masing sebanyak 99,32% dan 99,31%. Klorometilasi C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena dan C-3,4-dimetoksifenilkaliks[4]resorsinarena menggunakan paraformaldehida, ZnCl₂, HCl dalam N,N-dimetilformamida (DMF) menghasilkan klorometil-C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena dan klorometil-C-3,4-dimetoksifenilkaliks[4]resorsinarena sebanyak 88,05% dan 80,71%. Selanjutnya reaksi dengan trifenilfosfin menghasilkan C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida dan C-3,4-dimetoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida yang bermuatan positif dengan rendemen sebesar 96,40% dan 97,14%, secara berturut-turut.

Adsorpsi Cr(VI) pada C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida dan C-3,4-dimetoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida terjadi pada pH optimum 4 pada waktu kontak 180 dan 30 menit dengan kapasitas adsorpsi sebesar 24,37 mg/g dan 15,71 mg/g serta $\Delta G^\circ = -28,76$ kJ/mol dan $-36,24$ kJ/mol, secara berturut-turut. Kemudian adsorpsi RBBR pada

C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida dan C-3,4-dimetoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida terjadi pada pH optimum 10 dengan waktu kontak 360 menit, kapasitas adsorpsi sebesar 37,61 mg/g dan 132,09 mg/g, dan $\Delta G^\circ = -27,12$ kJ/mol dan $-26,94$ kJ/mol. Selanjutnya, adsorpsi DBS pada C-4-etoksi-3-metoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida dan C-3,4-dimetoksifenilkaliks[4]resorsinarena trifenilfosfonium klorida terjadi pada pH optimum 8 dengan waktu kontak 120 menit, kapasitas adsorpsi sebesar 11,53 mg/g dan 12,93 mg/g, dan $\Delta G^\circ = -23,83$ kJ/mol dan $-24,87$ kJ/mol, secara berturut-turut. Semua proses adsorpsi yang terjadi mengikuti model kinetika orde kedua semu Ho dan McKay, isoterm adsorpsi Langmuir, dan terjadi secara kemisorpsi.

Kata kunci: kaliks[4]resorsinarena bermuatan positif, adsorpsi, kemisorpsi, Cr(VI), RBBR, dan DBS.

SYNTHESIS OF C-ALCOXYPHENYL CALIX[4]RESORCINARENE TRIPHENYLPHOSPHONIUM CHLORIDE SERIES AND ITS USE AS ADSORBENT FOR Cr(VI), REMAZOL BRILLIANT BLUE R (RBBR), AND SODIUM DODECYLBENZENE SULFONATE (DBS)

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ABSTRACT

Synthesis of a new positively-charge calix[4]resorcinarene, C-alkoxyphenyl-calix[4]resorcinarene triphenylphosphonium chloride series has been conducted. The synthesis was carried out from vanillin (4-hydroxy-3-methoxybenzaldehyde) via ethylation, aromatic electrophilic substitution-cyclization, chloromethylation, and bimolecular nucleophilic substitution reactions. Structural elucidation of products was performed using FTIR and NMR spectrophotometer, SEM and BET. Positively charged of calix[4]resorcinarene, C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride and C-3,4-dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride were then used as anionic water pollutant adsorbent: hexavalent chromium (Cr(VI)), Remazol Brilliant Blue R (RBBR), and Sodium Dodecylbenzene Sulfonate (DBS). Adsorption parameters including pH, kinetic, and adsorption isotherm were also determined.

Reaction of 4-hydroxy-3-methoxybenzaldehyde with diethyl sulfate catalyzed by NaOH was performed by refluxing for 4 hours and gave 4-ethoxy-3-methoxybenzaldehyde in 99.16% yields. The aromatic electrophilic substitution-cyclization of ethylation and methylation products and resorcinol in the presence of HCl gave C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene and C-3-methoxyphenylcalix[4]resorcinarene in 99.32% and 99.31% yields. Chloromethylation of C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene and C-3-methoxyphenylcalix[4]resorcinarene using paraformaldehyde, ZnCl₂, HCl in N,N-dimethylformamide (DMF) produced chloromethylated C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene and C-3,4-dimethoxyphenylcalix[4]resorcinarene (88.05% and 80.71% yields). Then, reacted with triphenylphosphine to give positively-charged C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride and C-3,4-dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride in 96.40% and 97.14% yields, respectively.

Adsorption of Cr(VI) on C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride and C-3,4-dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride occurred at optimum pH 4 with a contact time of 180 and 30 minutes, adsorption capacities of 24.37 mg/g and 15.71 mg/g, and $\Delta G^\circ =$

-28.76 kJ/mole and -36.24 kJ/mole, respectively. Furthermore, adsorption of RBBR on C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride and C-3,4-dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride occurred at optimum pH 10 with a contact time of 360 minutes, adsorption capacities of 37.61 mg/g and 132.09 mg/g, and $\Delta G^\circ = -27.12$ kJ/mole and -26.94 kJ/mole. Then, adsorption of DBS on C-4-ethoxy-3-methoxyphenylcalix[4]-resorcinarene triphenylphosphonium chloride and C-3,4-dimethoxyphenylcalix[4]-resorcinarene triphenylphosphonium chloride occurred at optimum pH 8 with a contact time of 120 minutes, adsorption capacities of 11.53 mg/g and 12.93 mg/g, and $\Delta G^\circ = -23.83$ kJ/mole and -24.87 kJ/mole, respectively. All adsorption following the pseudo second order kinetic model of Ho and McKay, Langmuir adsorption isotherm, and chemisorption.

Keywords: positively-charged calix[4]resorcinarene, adsorption, chemisorption, Cr(VI), RBBR, and DBS.