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Electrokinetic Remediation of Contaminated Soil Enhanced by Cyclodextrins

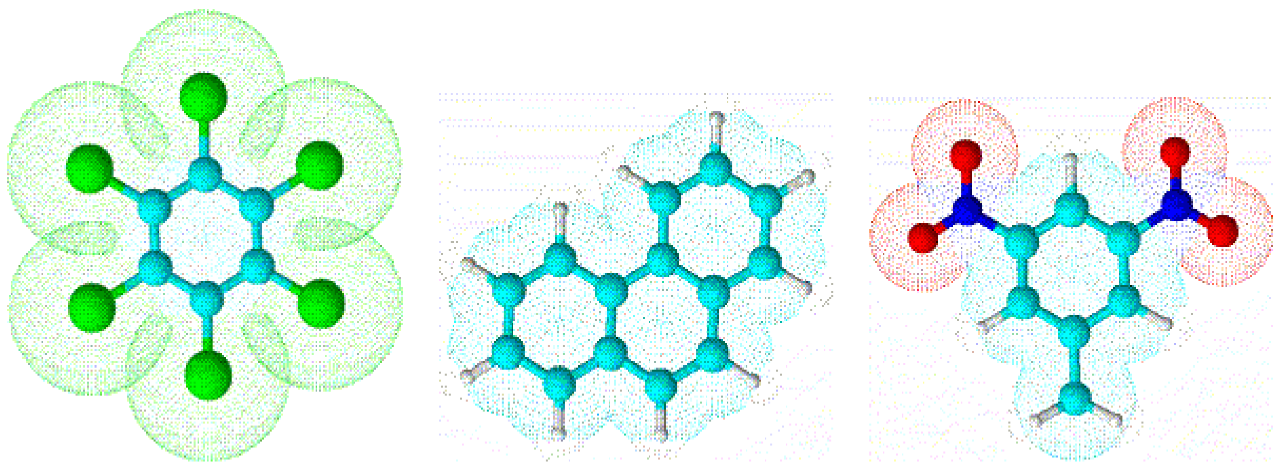
Recent research has shown that electrokinetic remediation is one of the promising technologies for the remediation of low permeable soil. In this process, the contaminants are separated by the application of electric field between two electrodes inserted in the contaminated mass. The electric field initiates certain transport mechanisms such as electromigration, electro-osmosis and electrophoresis in the soil that involve the movement of ions, pore fluid and charged particles, respectively in the medium (Oonitan et al., 2008). Electro-osmosis is the key transport phenomenon for the removal of organic contaminants in soils, sludge and sediments (Cameselle and Reddy, 2012).

This process removes metals and polar organic contaminants from low permeability soil, mud, sludge, and marine dredging by applying electric current. The technology is primarily a separation and removal technique for extracting contaminants from soils, which can be combined by other remediation technologies (Huang et al., 2012, Pazos et al., 2010).

Electrokinetic remediation can be implemented both *in situ* and *ex situ* to remove both heavy metals and organic contaminants from the soil and sediments. Electrodes are installed in the soil, and a low electric potential is applied across the anodes and the cathodes to induce electromigration (the movement of ionic species toward the oppositely charged electrode) and electrophoresis (the movement of charged colloids to the oppositely charged electrode) (Reddy and Ala 2006). Applying direct current to the soil the temperature is enhanced, which helps to desorb the organic contaminants and volatilize them. The efficiency of electrokinetic remediation is in close relationship with the mobility (solubility and/or adsorption to the soil) of the contaminants. Any additives that improve the solubility and desorption of pollutants (surfactants, co-solvents, chelants and cyclodextrins) will enhance the efficacy of the technology. Charged cyclodextrins help the removal even of the apolar organics such as PAHs by complexing them.

Some examples are given below to illustrate how CDs can enhance the electrokinetic remediation.

BCD showed a positive effect (higher than Tween 80) on the electrokinetic removal of hexachlorobenzene (HCB) (Yuan et al. 2006), while it was found to have a negative effect in the case of di- and trichlorobenzene, as the complexes of the latter compounds with BCD have lower solubility than the uncomplexed ones (Yuan et al. 2007). BCD was found to be a proper flushing agent of HCB enhancing successfully the removal from kaolin as model clayed soil by electrokinetic flushing combined with electrokinetic redox reaction with hydrogen peroxide reaching over 60% removal rate in 2 weeks (Oonitan et al., 2008).



Scheme of hexachlorobenzene, phenanthrene and 2,4-dinitrotoluene

The water-soluble cyclodextrin derivatives improve the solubility of most of the organic soil pollutants thus ensure the necessary mobility for electrokinetic remediation. For instance, a three-fold enhancement in the efficacy of electrokinetic removal of phenanthrene was achieved in the presence of 1% HPBCD, due to the improved solubility (Ko et al. 2000). Applying 10% HPBCD was beneficial for the migration of phenanthrene toward the cathode in a low-permeability soil (Maturi and Reddy 2006). Charged CD derivatives, such as carboxymethyl CD (CMBCD) can enhance the transport of the organic contaminants even more (Jiradecha et al. 2006). Due to the high solubilizing effect and the negative charge, CMBCD doubled the electrokinetic removal of naphthalene and 2,4-dinitrotoluene. Glycin-βCD was also successfully used combined with pH control for the electrokinetic removal of phenanthrene and atrazine (Wang et al., 2012 and 2012a).

Methyl βCD (MeBCD) was compared with cosolvent in removal of HCB from contaminated sediment (Wan et al., 2009). Test with 50% ethanol exhibited the highest performance, followed by test with 50 g L^{-1} MeBCD. The performance of HCB removal for tests with varied solubilizing agents was a combined effect of the distribution of solubilizing agents in sediments, the dissolution of HCB by pore liquid and the cumulative electroosmotic flow. Taking into consideration the detrimental impact of the 50% ethanol solution on the soil microflora the use of MeBCD was proposed.

CDs are non-toxic, biodegradable and leave no secondary pollutants (Fenyvesi et al., 2005). Since bacterial surface generally carries negative charge, the microbes are migrating under the applied voltage. The biodiversity of the microbial community in soil is usually reduced following electrokinetic remediation. The technology parameters should be carefully selected to achieve optimal removal rate without high loss in biomass. At 200 Vm^{-1} for 10 days, 36% petroleum hydrocarbons (TPH) were removed, with a small population of microbial cells flushed out, demonstrating that elektrokinetic remediation is effective for the oil-contaminated soils collected in field without marked effect on the microflora (Wan et al., 2011).

Applying HPBCD can help the electrokinetic removal as well as the bioremediation (bioavailability of the contaminants) in a combined technology (Sun et al., 2012).

The effect of CD depends on the soil properties: 20% and 94% of 2,4-dinitrotoluene could be removed from a soil with a high organic content and from a clayed soil, respectively, applying a 2% HPBCD solution (Khodadoust et al. 2006). The difference is explained by the strong adsorption of the contaminant to the organic content of the soil. The adsorption depends on the chemical nature of contaminant as well: phenanthrene was easily removed compared to HCB by HPBCD-enhanced electrokinetic remediation (Pham et al., 2010).

The CD solution can be regenerated by combining electrokinetic extraction with other remediation technologies, such as bioremediation or in situ chemical oxidation (Gomez et al., 2010).

In some cases electrokinetic remediation was unsuccessful due to the reduced desorption of the contaminants (PAHs and toxic metals) from the sediments and soils of high organic material content and of high buffering capacity. Only slight improvement was achieved by both 10% HPBCD and 3% Tween 80 solutions (Reddy and Ala 2006; Reddy et al. 2006). HPBCD also failed to improve the electrokinetic removal of metals in other experiments and in the case of real aged sediment (Reddy and Ala 2005, Li et al., 2009).

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Pulmonary Administration of a Water-Soluble Curcumin Complex Reduces Severity of Acute Lung Injury

HPGCD, Calu-3 human airway epithelial cell monolayers, murine model, markers of inflammation, oxidant stress

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Folate-appended ss-cyclodextrin as a promising tumor targeting carrier for antitumor drugs in vitro and in vivo

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4. CDs in Cell Biology

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immortalised hypothalamic neurons, transfection efficiency

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Self-assembling Modified beta-Cyclodextrin Nanoparticles as Neuronal siRNA Delivery Vectors: Focus on Huntington's Disease.

modified amphiphilic BCD, cerebrospinal fluid, rat striatal cells, HD primary fibroblasts

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heptakis[2-(?-amino-oligo(ethylene glycol)) -6-deoxy-6-hexadecylthio]-BCD, heptakis[2-(?-amino-oligo (ethylene glycol))-6-deoxy-6-dodecylthio]-BCD, bilayer vesicles, micelles, gene delivery

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Cyclodextrins for non-viral gene and siRNA delivery.

monodisperse functionalised CDs, targeting, polymer backbone, dendrimeric vector, polyrotaxane

O'Mahony, Aoife M.; O'Neill, Martin J.; Godinho, Bruno M. D. C.; Darcy, Raphael; Cryan, John F.; O'Driscoll, Caitriona M.: (2013) Pharmaceutical Nanotechnology 1(1), 6-14

5. CDs in Food, Cosmetics and Agrochemicals

Food-packaging sheet.

tannin, hesperidin, water-soluble peptide, BCD, GCD, tea bags

Hanaoka, Koji; Murata, Moriyasu.: (2013) JP2013035577A, 2013/02/21/ Jpn. Kokai Tokkyo Koho, 14pp.

Moisture diffusivity in food materials.

glucose homopolymers, Darken relation, Stokes- Einstein relation, free vol. theory, hydrophilic biopolymers found in food

van, der Sman, R. G. M.; Meinders, M. B. J: (2013) Food Chemistry 138(2-3), 1265-1274

Comparative study of flavor in cholesterol-removed Gouda cheese and Gouda cheese during ripening

milk treated with cross-linked BCD, Free fatty acids

Jung, H.J.; Ganesan, P.; Lee, S.J.; Kwak, H.S.: (2013) Journal of dairy science

Encapsulation of natural flavors in cyclodextrins: free volume studies by PALS.

garlic, marjoram, mechanisms for the encapsulation

Marques, M. F. Ferreira; Gordo, P. M.; Santos, S. D.; Marques, R. F. ; Moreira, da Silva, A.; Kajcsos, Zs: (2013) Materials Science Forum 733(Positron and Positronium Chemistry X), 88-91

Multilayered antimicrobial edible coating and its effect on quality and shelf-life of fresh-cut pineapple (Ananas comosus).

antimicrobial complex, BCD and trans-cinnamaldehyde, dipping method

Mantilla, N. ; Castell-Perez, M. E. ; Gomes, C. ; Moreira, R. G.: (2013) LWT--Food Science and Technology 51(1), 37-43

6. CDs for other Industrial Applications

Cyclodextrin or its derivative metal complex, its synthesis method and application in preparing biodiesel.

catalyst, animal or plant crude oil, interesterification, stability

Yang, Song; Chang, Fei; Xue, Wei; Wang, Rui; Hu, Deyu; Wu, Zhibing; Jin, Linhong; Qin, Wenting; Wang, Zhongbo.: (2013) CN102935383A, 2013/02/20/ Faming Zhuanli Shenqing, 13pp.

Syntheses of Metallic Cyclodextrins and Their Use as Synergists in a Poly(Vinyl Alcohol)/Intumescent Flame Retardant System.

Maleated cyclodextrin, polyphosphate, DTG, intumescent char, SEM, FTIR, XPS

Feng, Jianxiang; Zhang, Xiaomin; Ma, Songqi; Xiong, Zhu; Zhang, Chuanzhi; Jiang, Yanhua; Zhu, Jin: (2013) Industrial & Engineering Chemistry Research 52(8), 2784-2792

Chemical-microbial combined repair method for polycyclic aromatic hydrocarbon- and heavy metal-compositely polluted site soil.

Me beta- cyclodextrin, ultrasonically treating, inoculating

Luo, Yongming; Sun, Mingming; Teng, Ying; Liu, Wuxing; Li, Zhengao: (2013) CN102941225A, 2013/02/27/ Faming Zhuanli Shenqing, 8pp.

Antibacterial anti-aging protective sleeve of mobile telephone shell, and its preparation method.

chitosan, tea polyphenol, CM-cellulose, BCD, dust-proof, hygiene, heat resistance, cold resistance, biodegradable, environmentally friendly

Pang, Jie; Li, Mengfan; Li, Yaoling; Lan, Run; Sun, Zhongqi; Ye, Weijian; Wang, Jie.: (2013) CN102942713A, 2013/02/27/ Faming Zhuanli Shenqing, 7pp.

Method for reducing foreign odor of sulfur-vulcanized rubber product.

reducing odor of sulfur-vulcanized rubber product

Wang, Congzhou; Wu, Shengli; Feng, Shulin.: (2013) CN102942717A, 2013/02/27/ Faming Zhuanli Shenqing, 7pp.

Continuous Separation of alpha-Cyclohexyl-mandelic Acid Enantiomers by Enantioselective Liquid-Liquid Extraction in Centrifugal Contactor Separators: Experiments and Modeling.

hydroxyphenyl-BCD, extn. efficiency, multistage model

Tang, Kewen; Zhang, Hui; Zhang, Panliang: (2013) Industrial & Engineering Chemistry Research 52(10), 3893-3902

Dynamic interactions between cyclodextrin, an organic pollutant, and granular activated carbon in column studies

trichloroethylene, HPBCD, retardation factor, flow rate

Blanford, WJ Gao, H: (2012) J. Environ. Monit. 2012, 14, 11, 3024-3028

Enantioselective separation of chiral aromatic amino acids with surface functionalized magnetic nanoparticles

carboxymethyl-BCD, enantiomeric excess, FTIR, spectroflurometry

Ghosh, Sudipa ; Fang, Tan Hui ; Uddin, M.S. ; Hidajat, K.: (2013) Colloids and surfaces. B, Biointerfaces 105C, 267-277

Beta-Cyclodextrin-based oil-absorbent microspheres: Preparation and high oil absorbency.

octadecyl acrylate, Bu acrylate, 2,2'-azoisobutyronitrile, PVA

Song, Ci; Ding, Lei; Yao, Fei; Deng, Jianping; Yang, Wantai.: (2013) Carbohydrate Polymers 91(1), 217-223

Lipase-catalyzed synthesis and characterization of polymers by cyclodextrin as support architecture.

chaperone, polytransesterification, BCD

Liu, Wenhui; Wang, Fang; Tan, Tianwei; Chen, Biqiang.: (2013) Carbohydrate Polymers 92(1), 633-640

Unique catalytic effect of a cyclodextrin host on photodimerization of coumarin in nonpolar solvents.

Heptakis(6-O-tert-butyldimethylsilyl)-BCD

Asahara, Haruyasu; Iwamoto, Takuya; Kida, Toshiyuki; Akashi, Mitsuru.: (2013) Tetrahedron Letters 54(7), 688-691

7. CDs in Sensing and Analysis

Synthesis of cyclodextrin-silicate sol-gel composite embedded gold nanoparticles and its electrocatalytic application

determination of nitroaromatics

Manivannan, S Ramaraj, R: (2012) Chem. Eng. J, 210, 195-202

Using a novel sol-gel stir bar sorptive extraction method for the analysis of steroid hormones in water by laser diode thermal desorption/atmospheric chemical ionization tandem mass spectrometry

polydimethylsiloxane/phenyltrimethylsiloxane/BCD sol-gel material

Duy, SV Fayad, PB Barbeau, B Prevost, M Sauve, S: (2012) Talanta 101, 337-345

Strategy for Polychlorinated Biphenyl Detection Based on Specific Inhibition of Charge Transport Using a Nanogapped Gold Particle Film

inhibition of charge transport, BCD, modified "thermionic emission" electron tunneling model

Yu, Y Chen, X Wei, Y Liu, JH Huang, XJ: (2012) Anal. Chem. 84 (22), 9818-9824

Determination of enantiomeric composition of ibuprofen in pharmaceutical formulations by partial least-squares regression of strongly overlapped chromatographic profiles

permethyl-BCD chiral column

Grisales, JO Arancibia, JA Castells, CB Olivieri, AC: (2012) J. Chromatogr. B 910, 78-83

Recent advances in electrodriven enantioseparations.

chiral selectors, review, math. modeling

Jac, Pavel; Scriba, Gerhard K. E.: (2013) Journal of Separation Science 36(1), 52-74

Stereoselective quantitation of mecoprop and dichlorprop in natural waters by supramolecular solvent-based microextraction, chiral liquid chromatography and tandem mass spectrometry.

sepn. of target enantiomers on a permethylated ACD chiral column

Caballo, C.; Sicilia, M. D.; Rubio, S.: (2013) Analytica Chimica Acta 761, 102-108

Synthesis of a novel cyclodextrin-derived chiral stationary phase with multiple urea linkages and enantioseparation toward chiral osmabenzene complex.

immobilizing heptakis(6- azido-6-deoxy-2, 3-di-O-p-chlorophenylcarbamoylated) -BCD onto silica gel, osmabenzene, HPLC, NMR

Lin, Chun; Liu, Wenna; Fan, Jun; Wang, Yuekui; Zheng, Shengrun; Lin, Ran; Zhang, Hui; Zhang, Weiguang: (2013) Journal of Chromatography, A 1283, 68-74

Selective separation of deltamethrin by molecularly imprinted polymers using a beta-cyclodextrin derivative as the functional monomer.

bis(-6-O-butanediacid monoester)-BCD, toluene 2, 4-diisocyanate, selective recognition, solid phase extn.

Xu, Zhi F.; Wen, Ge; Kuang, Dai Z.; Zhang, Fu X.; Tang, Si P: (2013) Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes 48(5), 336-343

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