



Research article

Radiation induced *in-situ* cationic polymerization of polystyrene organogel for selective absorption of chlorophenols from petrochemical wastewater



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ABSTRACT

A new *in-situ* cationic polymerization was performed to synthesize a cross-linked (91%) polystyrene (PS) organogel through tetrachloroethylene radiolysis assisted by ⁶⁰Co gamma rays. Hoernschemeyer diagram and swelling capacity test show a better selectivity of PS organogel to chlorinated molecules compared to ester, hydrocarbons and alcohols organic molecules by 80–184 folds. Response surface modeling (RSM) of CPs (2,4,6-trichlorophenol) sorption from artificial wastewater confirm superiority of PS organogel to absorb 1746 μmol CPs/g (~345 mg CPs/g) at broad pH (4–10) and temperature (25–45 °C). Based on ANOVA statistic, simulated CPs absorption model onto PS organogel was successfully developed, with accuracy of prediction of $R^2 \approx R^2_{Adj}$ of 0.991–0.995 and lower coefficient of variation of 2.73% with F_{model} of 611.4 at $p < .0001$. Particularly, the usage of PS organogel for petroleum wastewater reclamation exhibited higher absorption affinities for all the organic contaminants especially for CPs (>99%) by non-covalent and/or dispersive interaction mechanisms with a well-term reusability and good stability up to 5 cycles.

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1. Introduction

Removal of chlorophenols (CPs) pollutants from water bodies has been a challenge for a long time, due to their high polarity, water solubility and toxicity effect even at their lowest concentrations (above environmentally quality standard “EQS” of 20–50 μg/L). Resulting from the increasing influence of population growth and societal activities, CPs contamination has become a problem of high priority in discharged wastewater from petroleum (*i.e.* refinery and petrochemical), paint, coal conversion, and pesticide industries, among others (Li et al., 2012; Păcurariu et al., 2013). Adsorption, one of wastewater remediation procedures, is an effective treatment method because of its easy application for a wide range of pollutants and economic regeneration operation

compared with others procedures, especially if the pollutants have to be recycled. To date, a huge number of synthetic adsorbents have been used to promote the features of the organic pollutant adsorption (Fathy et al., 2017; Li et al., 2012; Younis et al., 2016; Younis and Moustafa, 2017). Compared to the traditional adsorbents (such as activated carbon, nanocomposites, hybrid organic-inorganic materials, carbon nanomaterials, nanomaterials, etc.), a promising direction of research was focused on the synthesis of an entirely hyper cross-linked nano-polymeric sorbents, such as macroporous copolymers, for selective and/or urgent purification and recovery of specific contaminant from wastewaters (El-hoshoudy et al., 2017; Păcurariu et al., 2013; Xiao et al., 2017; Younis et al., 2017; Zhang et al., 2017).

The development of new selective polymeric materials to clean-up wastewater effluents with improved selectivity for chlorinated-organic pollutant is important in order to enhance their potential for instant wastewater cleaning and molecular recovery processes. In fact, the hyper cross-linked polystyrene (PS) polymer, represent a third generation of polystyrene material, in addition to traditional

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gel-type and macroreticular copolymers (Susoff and Oppermann, 2009; Tsyurupa et al., 1995). Therefore, from the polymer point of view, gels made of hyper cross-linked PS polymer in a more controlled manner (via γ -rays) than those synthesized via chemical cross-linking copolymerization is expected to build a new PS sorbent material for perfect substrate/solute uptake, recovery and reusability with excellent sorption/desorption properties and stability. However, preparation of highly cross-linked polystyrene (PS) organogel with high molecular uptake performances and regeneration efficiency puzzled researchers for a long time until now (Davarpanah et al., 2015; Lin et al., 2012).

As known, a gel is a soft solid or solid-like formulation consisting of two or more components, one of which is a liquid phase in a network (that could be nonpolar (organogel) or polar (hydrogel)), present in substantial quantity, according to Kramer's definition (Zhang et al., 2017). Gelation occurs through the cross-linking of polymer chains, something that can be achieved by: (i) covalent bond formation (chemical cross-linking), or (ii) non-covalent bond formation (physical crosslinking) (Sagiri et al., 2014; Zhang et al., 2017). For this purpose, owing to the features of gamma (γ) radiation, as a clean and economic innovative technology, γ -radiation to create polymeric adsorbent is now under researchers' interest. To the best of our knowledge, the potential application of γ -ray for the synthesis of cross-linked PS organogel by free radical polymerization mechanism is still limited and shows difficulties. On the other side, some works dealing with the effect of gamma-ray irradiation have shown the possibility in chlorinated solvents of radiation-induced cationic polymerization of styrene (Chapiro, 1979; Egusa et al., 1977; Wang and Dorfman, 1980). The polymerization can be done via either cationic or combined of cationic radical polymerization (Broltow, 2004).

In this study, therefore, we report the potential fabrication of highly stable hyper cross-linked PS organogel using γ -ray irradiation in the presence of tetrachloroethylene solvent as a novel green synthetic procedure. The degree of crosslinking of the developed PS organogel by γ -rays as well as hydrophobic and swelling behavior in polar and nonpolar solvents were studied. In addition, we investigated and optimized the capacities of the PS organogel for selective CPs absorption from synthetic petroleum wastewater effluents at different operating parameters (such as pH, CP concentrations, temperature, PS amount, and absorption time) using response surface methodologies (RSM). Furthermore, potential applicability and recyclability tests were carried out for decontamination of real petroleum wastewater effluent, in order to evaluate the economical used of the PS organogel in practical case studies.

2. Experimental methodology

2.1. Radiation induced cationic polymerization of PS organogel

In this procedure, 5 g of polystyrene pellets were dissolved in 25 mL of tetrachloroethylene. Viscous solution of polystyrene was transferred into glass tubes and then irradiated in ^{60}Co Gamma Cell at dose 20 kGy with a dose rate of 2.02 kGy/h at ambient conditions. The outcome of cylindrical PS organogel sample were cut into disks and dried at room temperature and then crushed.

The details of materials and characterization procedures of the synthesized PS organogel material as well as measurement of swelling (g/g) and gel fraction (%) are listed in the [Supporting Information](#).

2.2. Application of PS organogel for absorption of CPs from wastewater solutions

Experimental absorption capacities of CPs like "2,4,6-trichlorophenol" by the synthesized PS organogel sorbent were determined by batch procedure. In each experiment, a known amount of PS absorbate was suspended in 50 mL of wastewater solution (Total dissolved solids (TDS) \approx 1000 mg/L) at a known CPs concentration in a sealed flask, and agitated with speed rate of 150 rpm. The effect of operating parameters, including pH ($X_1 = 4\text{--}10$), CPs concentrations ($X_2 = 1\text{--}5$ mmol), water temperature ($X_3 = 25\text{--}45$ °C), PS amounts ($X_4 = 5\text{--}15$ g/L) and absorption time ($X_5 = 0.5\text{--}3$ h) were studied using RSM-optimal design of experiments (RSM-ODE). Absorption parameters were varied over three-levels according to the RSM-ODE matrix shown in [Table S1](#) simulated by the Minitab (version 17, USA) software. At the end of each absorption experiment, the PS gel sorbent was collected by centrifugation and the residual CPs concentration was determined by a Jeanway UV-6500 spectrophotometer at 286 ± 5 nm. Positive blank sample without PS organogel was tested under the same experimental conditions to evaluate the stability of CPs solution. Each experiment was done in triplicate under identical conditions (S.D. $\approx \pm 1.07\%\text{--}3.2\%$). The experimental PS gel absorption capacities for CPs (q_e $\mu\text{mol/g}$) were calculated with equation (1) of

$$q_e = \frac{C_o C_t}{M} \times V \quad (1)$$

where C_o and C_t are the CPs concentrations ($\mu\text{mol/L}$) in water solution before and after treatment, respectively, V (L) is the volume of wastewater, and M (grams) is the mass of PS organogel sorbent.

3. Results and discussion

In this work, the main initiating species of in-situ cationic polymerization of PS organogel are considered to be monomer cationic species produced by γ -irradiation. Different trials for the synthesized of the PS organogel were firstly performed using several organic solvents such as toluene, dimethylformamide (DMF), Tetrahydrofuran (THF), butanone, benzene, o-xylene, 1,4 dioxan and tetrachloroethylene as reaction media to promote the in-situ cationic polymerization under γ -rays. The primary results showed that the formation of linear PS organogel was not observed when using toluene, DMF, THF, butanone, benzene, o-xylene, or 1,4 dioxan solvents, even with increasing the γ -rays dose up to 120 kGy. But, the highly cross-linked PS organogel was successfully obtained only by tetrachloroethylene as a reaction solvent at room temperature with a gel yield fraction of 91%. In such case, we suggest that the γ -radiolysis of tetrachloroethylene liberates: i) chloride ions (Cl^-), ii) carbonium species (C^+) that act as Lewis acid species (Chapiro, 1974; Sutherland and Spinks, 1959), and/or iii) cationic radicals ($\text{C}^{\bullet+}$) species (Popova et al., 1965; Rajesh et al., 2007; Yağci and Reetz, 1998), which can induce PS linear chain recombination (crosslinking) (Ghobashy and Elhady, 2017; Ghobashy and Khozemey, 2016; Younis et al., 2017) to initiate polystyrene organogel polymerization, as shown in Scheme (1).

The proposed *in-situ* cationic polymerization mechanism of linear polystyrene by γ -rays illustrated in Scheme (1) agreed quite well with the results of Ueno et al. (1966) and Sigwalt and Moreau (2006) for the polymerization of styrene in methylene chloride. Similarly, the resulted Cl^- from the radiolysis of tetrachloroethylene by γ -rays promotes the formation of HCl and carbonium cation on styrene units which initiates a cationic polymerization of linear PS polymerization (Tsuda, 1961). The propagation step involved head-to-tail addition in carbocationic polymerization,

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