

Surface modification of monolithic PolyHIPE Polymers for anionic functionality and their ion exchange behavior

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ABSTRACT: Monolithic PolyHIPE Polymer (PHP), being a highly porous, low density, open cellular material was produced by polymerization of a high internal phase emulsion (HIPE) in which the polymerizable continuous phase consisted of monomers, styrene (STY), and divinyl benzene (DVB). The inner dispersed phase (90 vol %) was an aqueous solution containing 0.4 wt % potassium persulphate as initiator. The resulting porous structure had 12% crosslinking density. Surface chemistry of the monoliths was modified by chloromethylation and amination to impart anionic functionality. Surface modified monoliths had ion exchange capacity of 3.01 meq/g, and had the ability to uptake water about 10 times of its mass. It was used Cr (VI) ion removal from aqueous solution. The experimental results investigated for both the Langmuir and the Dubinin–Radushkevich adsorption models. The maximum Cr (VI) adsorptions are 126.6 mg Cr (VI)/g and 129.3 mg Cr (VI)/g, respectively. The mean free energy E of adsorption is 11.18 kJ/mol according to the Dubinin–Radushkevich adsorption model, indicating that the adsorption occurs through a chemical ion-exchange process and it is not diffusion limited. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42286.

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INTRODUCTION

PHPs represent a new class of cellular micro-porous materials with highly controllable physical and chemical structure.^{1–7} Functional PHPs are produced in three stages: (1) production of a HIPE with a polymerizable continuous phase and aqueous dispersed phase which constitutes more than 74 vol % of the total volume; (2) simultaneous polymerization and cross-linking of HIPE (and hence the acronymic name PolyHIPE) without separation of the phases; and (3) functionalization of the surface and/or the bulk of the pore walls.

Applications of PHPs are now extensive; they are used either as monolithic micro-reactors or in particulate form for chemical or biochemical conversions, or adsorbents as well as adsorbents or membranes or indeed as combination of these three basic modes of operation. In all these applications, the underlying characteristics for their function include controllability of pore volume fraction, surface area, pore size, three-dimensional connectivity

of the pores and the size of the interconnects, hierarchic pore, and interconnect structures and the chemical/biochemical functionality of the walls. Due to these attributes, PHPs and their metallic, ceramic or composite forms have been used in the emerging technology of Process Intensification (PI),⁸ which facilitates the establishment of green processes. In addition to use of PHPs in analytical sciences,⁹ the important specific applications of PHPs in PI include: Agro-PI,^{10–14} Bio-PI,^{15–17} Chemical-PI,¹⁸ including Separation processes,^{19–25} Energy and Environmental-PI,^{26–29} and medicine and tissue engineering.^{3,6,30,31} A recent review of some of these applications is available.³²

In most of the large scale applications of PHPs, such as agriculture^{10–14} and separation and energy-environmental processes,^{18–29} the bulk and surface functionality of PHP requires ion-exchange capacity. The required anionic or cationic characteristics are dictated by the nature of the application. Organic ion-exchanger media consists of a three-dimensional network of hydrocarbon chains which carry fixed ionic groups. Ionic

groups such as $-\text{SO}_3^-$ or $-\text{COO}^-$ in cation exchangers, and $-\text{NH}_3^+$ or $-\text{N}^+(\text{CH}_3)_3$ in anion exchangers are fixed within the matrix. The exchanger materials as resins or membranes are essentially crosslinked polyelectrolytes. They are insoluble, but can swell to a limited degree³³ depending on the cross-linking density. In some applications (such as in agriculture and environment), the total ion-exchange and water holding capacity of PHPs are paramount. Water holding capacity consists of two factors: ¹ void volume of PHP where absorption takes place and ² swelling capacity where adsorption takes place which requires hydrophilic walls. Therefore, the transformation of STY–DVB co-polymer into an ion exchange material not only induces hydrophilicity but it can also enhance adsorption capacity through swelling.

The most important difference between the commercial and PHP-based ion-exchangers is the accessibility of the ion-exchange sites in PHP which accelerates the exchange kinetics^{3,6,8,10–31} and allows the utilization of full exchange capacity.

STY/DVB copolymers are widely used in the preparation of many commercially available ion exchange resins as the precursor monomers. Three different methods have been used for the functionalization:^{2–4,6,34–38} ¹ the incorporation of the modification chemicals into the PHP at the emulsification stage (either in oil or aqueous phase or both) and after polymerization, functionalization of the incorporated chemicals,^{2–4,6,2} the copolymerization of a functional monomer with STY and DVB during the PHP formation,^{34–37} and ³ the grafting of a functionalized macromolecular chain on the wall of a previously prepared PHP.³⁸

Cation exchange PHPs have been used at large scale in agricultural and separation processes^{2,4,6,10–15,17,23–29} which resulted in large levels of intensification compared with the well established techniques. It is likely that in agricultural and separation processes as well as in biological applications, there is a real need for PHPs with anionic functionality. The absence of such anionic PHPs resulted in the lack of any progress in these areas. Therefore, in this present investigation we describe a method of producing anion exchange PHPs and characterize their ion-exchange capacity.

PHPs are prepared through a HIPE polymerization route, and hence the name which was coined at the Unilever Research Laboratories, Port Sunlight, UK^{1,39,40} where the material was originally developed by a team including one of us (GA). Subsequently, the principles of processing HIPEs have been established^{39,40} and used to obtain well characterized PHPs with predictable and uniform pore structures.^{3,4,6,8}

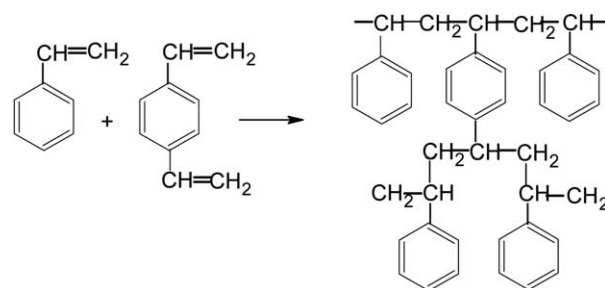
EXPERIMENTAL

Materials

STY, DVB, potassium persulphate, sorbitan monooleate (Span 80), chloromethyl methyl ether, pyridine, and isopropanol were purchased from Sigma Aldrich. Also, SnCl_2 , K_2CrO_4 , and 1, 5-diphenylcarbazide, used for equilibrium tests were Merck-reagent-grade chemicals.

Preparation of PHPs

In this work we used the method described in reference^{6,8} and based on the fundamental study reported by Akay^{39,40} for the



Scheme 1. Synthesis of PolyHIPE Polymer (crosslinked styrene/DVB copolymer).

HIPE preparation. The continuous oil phase of the HIPE was made from a mixture of STY crosslinked with DVB and a water-in-oil emulsifier, Span 80. The oil phase composition was STY 62%, DVB 23%, and Span 80 15% (by volume). The dispersed aqueous phase (internal phase) comprises a solution of polymerization initiator such as potassium persulphate (0.4% by mass), in distilled water. Enough amount of aqueous phase was dosed into the stirred oil phase until an aqueous to oil phase ratio of 90 : 10 (by volume) was achieved. The amount of internal phase was 54 ml. The mixing was carried out using two flat impellers perpendicular to each other so that the final level of the emulsion is about 1 cm above the top impeller. The lower impeller on the stirrer shaft is as close to the bottom surface of the vessel as possible. The processing conditions were: dosing rate of the aqueous phase, $R_D = 3$ ml/min, impeller speed, $\Omega = 300$ rpm, and total mixing time (including the dosing time) = 60 min.

As HIPE flows quite readily, it is easily polymerized in molds of any shape. After emulsification, the emulsion was transferred to cylindrical polyethylene containers and the emulsion was polymerized at 60°C for 4 h. PHP was produced as circular rods with diameters of 25 mm and lengths of 100 mm and then they were cut into discs (length of 4 mm). Once polymerized, washed, and dried, resulting PHP had 90% of void volume with 12% degree of crosslinking. Washing was performed using a Soxhlet equipment in isopropanol to remove unreacted monomers and the surfactant. Washing was continued with double distilled water. The reaction between STY and DVB proceeds according to the Scheme 1.

Chloromethylation of PHP Discs

The most commonly utilized neutral starting material in the preparation of a traditional hydrocarbon type ion exchange medium for industrial uses is STY–DVB copolymer. They form a strongly basic anion exchange resin which is usually prepared by two steps: chloromethylation and quaternary amination.^{33,34} Such a modification applied to the polymer matrix attaches positively charged groups its surface and alters from being hydrophobic to hydrophilic.

The chloromethylation of the polystyrene is a Friedel–Crafts condensation process catalyzed by anhydrous aluminum, zinc, or stannous chloride. About 10 g of crosslinked polystyrene was left in some volume chloromethyl methyl ether for 3 h. About 3 g of stannous chloride and 150 ml chloromethyl methyl ether were added to this mixture. Figure 1 presents the laboratorial

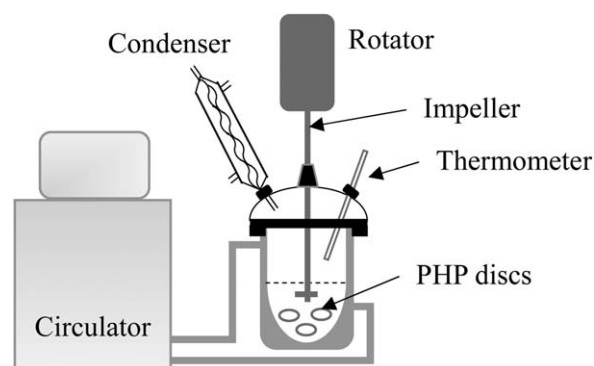


Figure 1. Schematic diagram of the apparatus used for chloromethylation and amination of PolyHIPE Polymer discs.

scheme utilized in the chloromethylation and amination of PHP discs. The mixture was placed in a round-bottomed flask, and then was stirred at 60°C for 12 h. Stirring was done slowly to prevent PolyHIPE discs from breaking up. The product was filtered and washed with distilled water and ethanol, and then was dried at 60°C for overnight under vacuum.

During chloromethylation, $-\text{CH}_2\text{Cl}$ groups were attached to the benzene rings of the crosslinked polystyrene chain. Scheme 2 shows the chemical structure of chloromethylated crosslinked polystyrene PHP represented as $\text{R}-\text{CH}_2\text{Cl}$.

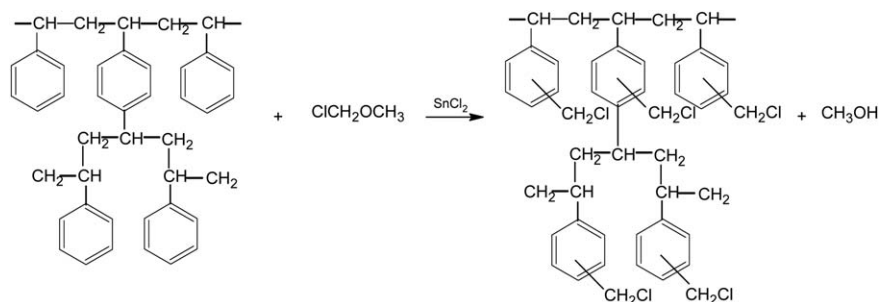
The chemical structure of chloromethylated crosslinked polystyrene PHP is described in Scheme 2 assuming that all the available benzene rings become chloromethylated (100% chloromethylated). However, 100% chloromethylation cannot be attained in PHP discs without sacrificing the mechanical integrity of the material since as chloromethylation proceeds, polymer starts swelling which in turn causes internal stresses leading to fracture of the polymer.

Amination of PHP Discs

The chloromethylated PHP (represented as $\text{R}-\text{CH}_2\text{Cl}$) was added 20 g pyridine, and then was stirred slowly at 100°C for 8 h. Then the discs were filtered and washed with 10% HCl and distilled water, and then were dried at 60°C for overnight under vacuum. A light yellow, disc shaped amino anion exchanger (Figure 2) was obtained. Scheme 3 shows the chemical structure of an anion exchanger PHP discs.

Characterization of Modified Polymers

In all of the analytical techniques, dried samples were used after the extraction of the surfactant and the residual monomers.



Scheme 2. Chloromethylation of PolyHIPE Polymer.

Scanning Electron Microscopy (Jeol 6400 scanning electron microscope) was used to observe the morphology of the PHP monoliths and to measure pore and interconnect sizes. Fourier Transform-Infrared (FT-IR) spectra of the modified surface were recorded on a Perkin-Elmer Spectrum One FTIR. A UV spectrophotometer (UV – 160 Shimadzu) was used to determine the chromate ion concentration in the determination of ion adsorption capacity of the modified PHP monoliths. The Brunauer-Emmett-Teller (BET) surface area of PHP monoliths were measured using a Beckman Coulter BET Gas Adsorption Analyser (Type SA310 Plus).

Equilibrium Water Absorption/Retention Capacity and Swelling Ratio of the Anionic Monoliths

The equilibrium water absorption capacity and swelling ratio of the anionic discs were determined after equilibrating sample in Cl^- ion form with distilled water at the room temperature. The disc samples were removed from the water and firstly weighed, and then measured their dimensions (diameter and height) immediately after blotting the free surface water. Then, they were dried at 60°C until constant dry weight was achieved. The water retention capacity (w_r) in unit gram $\text{H}_2\text{O}/\text{g}$ – dry monoliths (in Cl^- form) was deduced from the difference between the wet and the dry monoliths' masses based on the following formula

$$w_r = (w_w - w) / w \quad (1)$$

where w and w_w is dry and wet anionic PHP monolith mass, respectively. The swelling ratio (s_r) was determined directly from the ratio of wet volume (v_w) to dry volume (v), as follows:

$$s_r = v_w / v \quad (2)$$

Ion-Exchange Capacity (IEC)

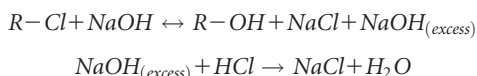
The usual capacity characterization of an ion exchanger is done by evaluating the number of ionogenic groups contained in the 'specific amount' of the material. The specific amount is defined as the amount which weighs one gram when the material is completely converted to the H^+ or Cl^- form and is free of sorbed solutes and solvents. So rigorous a definition is necessary because the weight of a given amount of the ion exchanger depends on the experimental conditions, for example, on its ionic form. The characteristic constant obtained in this way is usually called 'ion-exchange (or scientific weight) capacity' and is expressed in milliequivalents (meq) per gram.³³

After soaking in distilled water overnight, 1 g of powdered anionic PolyHIPE sample was immersed in 100 ml of 0.1 M NaOH aqueous solution for three days to reach equilibrium.



Figure 2. Photographic images of PolyHIPE Polymer discs before (left) and after transformation to an anion exchanger (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Then, a simple back titration technique was used to determine the number of Cl^- ions attached to the polymer chain. The titration reactions can be summarized as follows:



The ion exchange capacity of the anion exchanger PHP was calculated by

$$\text{IEC} = (m_0 - m_e) / w \quad (3)$$

where w is dry anion exchanger PolyHIPE mass (g) and m_0 and m_e are meq of NaOH in flask at the start and equilibrium, respectively.

The water holding capacity of PHP was determined after equilibrating sample of PHP in Cl^- ion form with distilled water at the room temperature. The PHP samples were removed from the water and weighed immediately after blotting the free surface water. They were then dried at 60°C until constant dry disc weight was achieved.

The water holding capacity (w_r) in gram water/gram – dry PHP (in Cl^- form) was deduced from the difference between the wet and the dry disc masses based on the following formula:

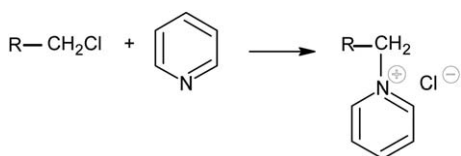
$$w_r = (w_w - w) / w \quad (4)$$

where w_w is wet anion exchanger PHP mass. The fixed ion concentration, c_r (meq/g- H_2O) was determined directly from the ratio of IEC to w_r , as follows

$$c_r = \text{IEC} / w_r \quad (5)$$

Equilibrium Ion Adsorption Tests on the Anionic PHP Monoliths

In the ion adsorption tests, the monoliths with 2.54 cm in diameter and about 0.3 cm in thickness were housed in a plastic module. In order to prevent leakage of the aqueous solution from the periphery of the monolith, the top of the module was



Scheme 3. Quaternary amination of chloromethylated PolyHIPE Polymer.

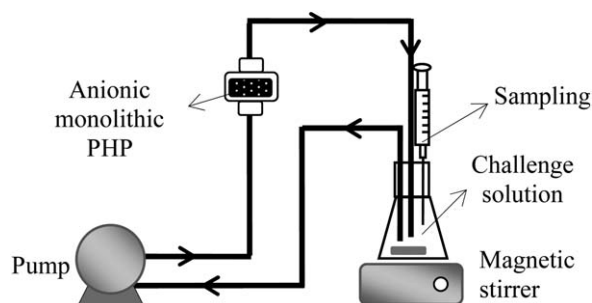


Figure 3. Schematic diagram of the apparatus used for ion adsorption tests

screwed into the sample holder. The leakage problem is further resolved as the anionic PHPs swell slightly when in contact with water, thus achieving self-sealing. For equilibrium ion adsorption tests, the stock solution of Cr (VI) was prepared by dissolving in deionized water appropriate amounts of reagent grade K_2CrO_4 . The tests were carried out at room temperature and at $\text{pH } 3.55 \pm 0.05$. An apparatus made entirely from plastic components was used to house the monoliths of known dry mass. The challenge solution (volume 300 ml) was circulated between the module and a stirred container via a peristaltic pump. The apparatus is shown schematically in Figure 3.

The concentration of chromate ions in the circulating solution was allowed to reach equilibrium, determined by periodic sampling (ca. 2 ml samples) of the solution. The concentration of chromate ions was determined with an UV – 160 Shimadzu spectrophotometer by measuring the absorbance of complex formed between diphenylcarbazide and chromate (for all hexavalent chromium species) at 540 nm.⁴¹ After steady state had been reached, the solution concentration was increased by adding a small concentrated sample of chromate solution. The mass of chromate on the anion exchanger PHP was calculated and isotherms showing the amount of chromate per gram of the anion exchanger PHP against the equilibrium concentration in the solution were evaluated.

The adsorption capacity of the anionic monoliths at equilibrium q_e (mg/g) was calculated by:

$$q_e = (c_0 - c_e) V / m \quad (6)$$

where, c_0 and c_e (mg/L) are the initial and equilibrium concentration of the chromate solutions respectively, V is the volume of chromate solution, and m is the mass (g) of the monolithic disc. After reaching the steady state and the addition of a small amount of concentrated chromate solution, the initially concentration and the volume of the mixture were recalculated.

RESULTS AND DISCUSSIONS

PHP Characterization

Figure 4 illustrates the morphology of the typical three-dimensional open-cellular structure of modified STY–DVB PHP which shows interconnected pores. Chemical modification does not alter the overall appearance of PHP. The formation of interconnects occurs because of shrinkage of thin monomer/surfactant walls during conversion to polymer.^{3,8} Provided that the oil phase and/or aqueous phase does not contain any fillers/

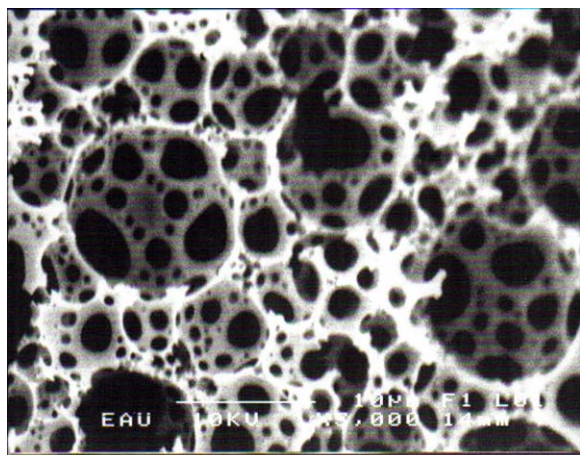


Figure 4. Scanning electron microscope of PolyHIPE Polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

additives including high levels of electrolyte during HIPE formation, the cell and interconnecting hole (interconnect) structures are typical of the primary cells as classified by Akay *et al.*³ There are no so called very large ‘coalescence pores’ because no additives/fillers were used at the HIPE formation stage.³

The pore size of PHP is approximately equals to the size of the aqueous phase droplets at the level of crosslinker and surfactant used in this study. Droplet size itself is mainly controlled by the emulsification temperature, dosing rate, mixing time, and impeller speed and total mixing time.^{3,6,8} Under the current processing conditions, pore size range was 8.5–12 μm and interconnecting hole size range was 0.4–3.5 μm as shown in Figure 4. These physical characteristics, evaluated using scanning electron microscopy (using dry samples) were not changed upon chemical modification although there was a slight increase in the BET surface area from 6.2 m^2/g to 7.6 m^2/g .

PolyHIPE as an Anion Exchange Material

Figure 5 shows the FTIR spectra of the aminated STY–DVB copolymer PHP with crosslinking density of 12%. In the multiple bond section from 1400 cm^{-1} to 2500 cm^{-1} the large number of absorptions between 1400 and 1800 indicate C– to –C o-

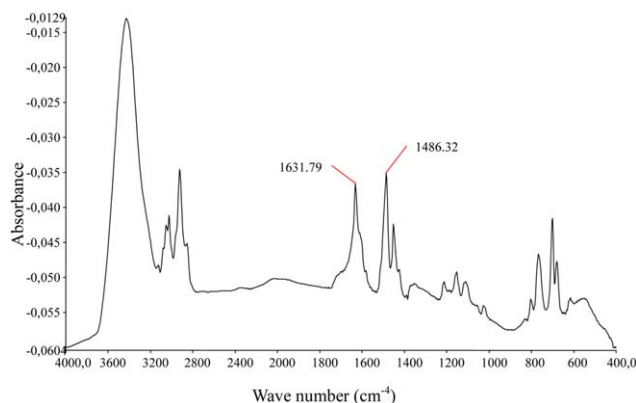


Figure 5. FTIR spectra of anion exchanger PolyHIPE Polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matic bonds. Two characteristic peaks at 1486 and 1631 cm^{-1} are attributed to pyridine groups and probably arises from stretching vibration of C=C and C=N bonds in pyridine ring, indicative of amination. From these measurements, it can be seen that pyridine reacted with the chloromethyl groups of the cross-linked PHP matrix.⁴²

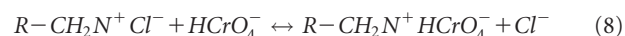
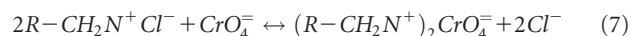
Water Uptake, Fixed Ion Concentration, and Ion Exchange Capacity

Titrimetric analysis determines the number of ionic groups for a given amount of resin (IEC); when in the Cl^- form this can be interpreted as the ‘total’ capacity. Total capacity is an important characteristic for ion exchanger medium. Anion exchanger discs have 3.01 meq/g total capacity. Characteristics of the anionic PHP are summarized in Table I in which the results are average of three samples.

When in contact with water the ion exchangers adsorb water into pores, partly as solvation shells of fixed, counter and co-ions, and partly as ‘free’ water. Swelling and water uptake and ion-exchange capacity are strongly dependent on the degree of crosslinking as high crosslinking density restricts swelling and the insertion of functional moieties responsible for ion-exchange.^{10–13} However, low crosslinking density results in mechanically weak material or the collapse of the porous PHP structure during polymerization. As a compromise,¹² in this study we used 12% crosslinking. Although chloromethylation also leads to additional crosslinking,³⁵ no attempt was made to estimate this additional crosslinking.

Equilibrium Ion Adsorption Tests

It is necessary to understand the solution chemistry of hexavalent chromium in order to explain the binding mechanism of chromate by the anionic PHP matrix. Different forms of Cr (VI) are found in the solution, and the relative proportions depended on both pH and total Cr (VI) concentration. The chromate may be represented in various forms such as H_2CrO_4 , HCrO_4^- , and CrO_4^{2-} , in the solution phase as a function of pH and concentration.⁴³ The sites responsible for the ion exchange process are due to the $-(\text{CH}_2) \text{N}^+ \text{Cl}^-$ groups in the anionic polymer matrix. An anion – exchange medium will absorb chromates from aqueous solution according to the reactions shown in the following equations:



The specie HCrO_4^- predominates⁴⁴ at low pH as 3.55 ± 0.05 . So, the mechanism of chromate ions adsorption on the anionic PHP can be given according to eq. (8).

The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir⁴⁵ and Dubinin–Radushkevich⁴⁶ (D–R) isotherm models. The linear forms of the Langmuir and Dubinin–Radushkevich (D–R) isotherm equations are represented by the following equations:

Langmuir equation

$$c_e/q_e = K_L/q_{\text{max}} + c_e/q_{\text{max}} \quad (9)$$

Dubinin–Radushkevich (D–R) equation

Table I. Ion Exchange and Water Uptake Capacities of the Anion Exchanger PHP

	IEC (meq/g-dry PHP)	w_r (g-H ₂ O/g-dry PHP)	C_r (meq/g-H ₂ O)	Swelling ratio S_r (-)	Dry density of PHP (g/ml)	Wet density of PHP (g/ml)
	3.01	10.6	0.284	1.16	0.085	0.863
SD ^a	0.111	0.409	0.011	0.069	0.006	0.134

^aStandard deviation.

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \quad (10)$$

$$\varepsilon = RT \ln(1 + 1/c_e) \quad (11)$$

The constant β gives an idea of the mean free energy E (kJ mol⁻¹) of adsorption per mol of the adsorbate when it is transferred to the surface of the solid from infinity in the solution, and can be calculated using the relationship:

$$E = (1/2\beta)^{1/2} \quad (12)$$

In the above equations, c_e is the equilibrium chromate ions concentration in solution (mg L⁻¹), q_e is the amount of chromate ions adsorbed at equilibrium (mg g⁻¹), q_{max} is the monolayer capacity of the adsorbent (mg g⁻¹), and K_L is the Langmuir constant and related to the energy of adsorption; β gives the mean free energy E of adsorption per mol of the adsorbate

(mol² kJ⁻²), when it is transferred to the surface of the solid from infinity in the solution. q_s is the theoretical saturation capacity (mg g⁻¹), ε is the Polanyi potential, R (J mol⁻¹ K⁻¹) is the gas constant, and T (K) is the absolute temperature.

The plots of c_e/q_e versus c_e (Langmuir) for the adsorption of chromate ions onto the monolithic anionic PHP [Figure 6(a)] give a straight line of slope $1/q_{max}$ and intercept K_L/q_{max} and by plotting $\ln q_e$ versus ε^2 [Figure 6(b)] (Dubinin–Radushkevich) it is possible to obtain the value of q_s from the intercept, and the value of β from the slope.

The Langmuir and D–R parameters for the adsorption of chromate ions onto anionic PHP monoliths are being listed in Table II. It is evident from these data that the adsorption of chromate ions onto the monoliths is fitted well with the Langmuir isotherm model than D–R isotherm models, as indicated by the r^2 values in Table II.

The Langmuir isotherm applies to sorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. It assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface.^{33,45} The maximum Cr (VI) adsorption is 126.58 mg Cr (VI)/g of weight the anionic PHP monolith. The maximum adsorption capacity of the anionic PHP monolith obtained for Cr (VI) in this study was found to be comparable and higher than those of many anion exchange resin reported in the literature.^{43,47}

The magnitude E is a useful for estimating the mechanism of the adsorption reaction. In the case of $E < 8$ kJ/mol, physical forces may affect the adsorption. If E is in the range 8 – 16 kJ/mol, adsorption is governed by ion exchange mechanism, while for the values of $E > 16$ kJ/mol, adsorption may be dominated by diffusion.⁴⁸ The numerical value of E was found to be > 8 kJ mol⁻¹, indicating that the adsorption may occur via a chemical ion-exchange process.

The preference of ion exchanger for one of the two counter ions is the so-called ‘separation factor’, defined as³³

$$\alpha_{Cl}^{Cr} = \frac{y_{Cr}}{x_{Cr}} / \frac{y_{Cl}}{x_{Cl}} \quad (13)$$

where y_i and x_i are respectively the ion fractions of species- i in the anionic PolyHIPE matrix and in the solution. If the ion chromate is preferred, the factor α_{Cl}^{Cr} is larger than unity, and if chloride is preferred, the factor is smaller than unity. The data reported in Figure 6 are reported in terms of ion exchange isotherm (a) and separation factor (b) in Figure 7.

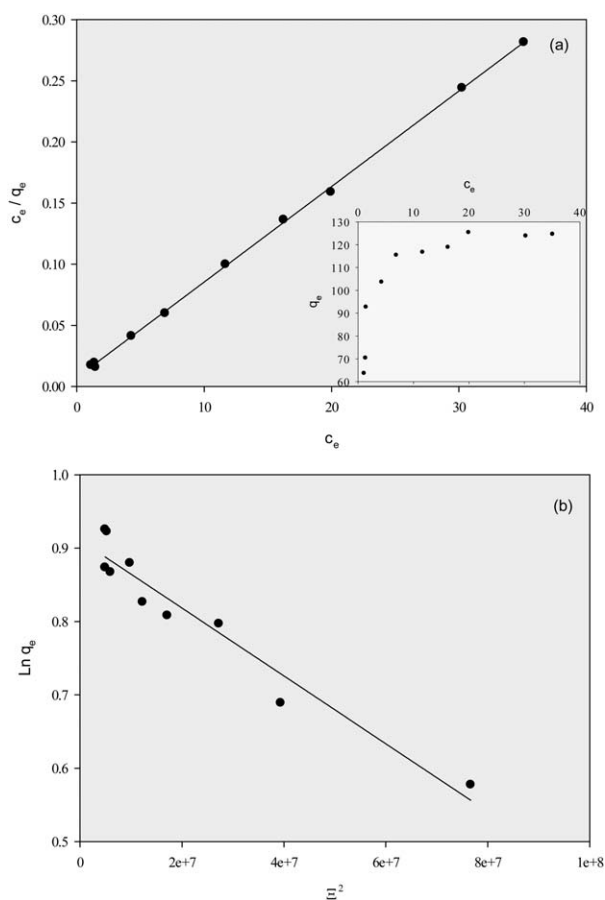
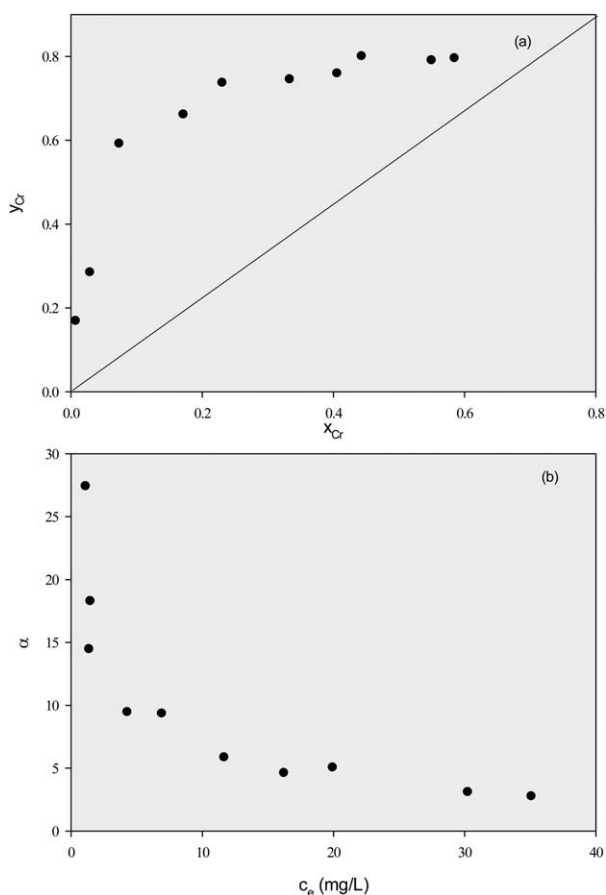


Figure 6. (a) Langmuir and (b) D – R plots for the adsorption of Cr (VI) ions by anionic PolyHIPE Polymer monoliths.

Table II. Isotherm Constants for the Adsorption of Chromate Ions onto Anionic PolyHIPE Polymer Monoliths

Langmuir	$c_e/q_e = 0.0079 * c_e + 0.0074$ $r^2 = 0.999$	q_{max} (mg Cr (VI)/g) 126.58	K_L (mg/L)	
			0.94	
D - R	$\ln q_e = -4 * 10^{-9} \varepsilon^2 + 0.9107$ $r^2 = 0.962$	q_s (mg Cr (VI)/g) 129.28	β (mol ² /J ²) $4 * 10^{-9}$	E (kJ/mol) 11.18

**Figure 7.** (a) Ion exchange isotherm and (b) separation factor plots for the adsorption of Cr (VI) ions by anionic PolyHIPE Polymer monoliths.

CONCLUSIONS

STY/DVB copolymers are widely used in the preparation of many commercially available ion exchange resins as the precursor monomers. Most of the commercial ion exchange resins are produced in bead form, usually between 0.5 and 1.5 mm in diameter, and therefore have relatively lower fluid to surface contact area ratios. To increase the surface area, beads of smaller diameter would have to be used which in turn cause a decrease in permeability of the exchange resin bed. The structure of PHP provides larger contact surface area with the benefit of higher permeability and circumvents diffusion limitation. The extended surface area and high permeability, together with the low mass of adsorbent material that arises as a result of the cellular structure of the media, make PHP very attractive as a potential adsorbent.

Monolithic PHPs are not easily chloromethylated and aminated due to the size of the interconnecting holes. However, by using

high internal phase volume, interconnect size is enhanced thus making it possible to modify the relatively thick sections of monolithic PHPs. The standard ionic states are hydrogen form and chloride form for cation and anion exchange resins, respectively, and to a fair approximation exchange capacity values can be predicted from the equivalent mass of the monomer characterizing the exchanger.^{9,49}

The empirical formula of the functional monomer for styrene amine PHP with 12% crosslinking density and in the chloride form may be written as $0.88 C_8H_6CH_2C_5H_5NCl + 0.12 C_{10}H_8CH_2C_5H_5NCl$. This yields a Relative Molecular Mass of 232.38. Therefore, theoretical maximum (assuming full amination) dry anion exchanger PHP in the chloride form will have 4.30 meq per dry gram of PHP. This theoretical value IEC of 4.30 meq/g-dry PHP is considerably larger than the experimentally obtained IEC of 3.01 meq/g-dry PHP, indicating that the amination is not 100%. There are several reasons for this incomplete amination, including steric hindrance during chlorination and amination, low diffusion rate of reactants to the reaction sites, high crosslinking density/low swelling level. However, these effects are also present more acutely in the commercial ion-exchange resins due to mm-levels of diffusion path, rather than μ m-level in PHP due to the presence of interconnecting holes in PHPs.

There was a stirrer within the apparatus (Figure 1) used for chloromethylation and amination of PHP monoliths, but stirring speed was adjusted very low to avoid breaking of the monoliths. The speed level may be inadequate for diffusion of the modification agents (chloromethyl methyl ether and pyridine) to the inside of the monoliths. It may be achieved more high values of IEC by more effective diffusion methods, as the agents to circulate from the monoliths. The potential of the PHP structure as an effective adsorbent is demonstrated, and would be enhanced if full IEC were achieved.

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