Hydrophobic–Hydrophilic Polydivinylbenzene/Polyacryldiethylenetriamine Interpenetrating Polymer Networks and its Adsorption Performance toward Salicylic Acid from Aqueous Solutions

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Hydrophobic–hydrophilic interpenetrating polymer networks (IPNs) composed of polydivinylbenzene (PDVB) and polyacryldiethylenetriamine (PADETA) were prepared and its adsorption performance toward salicylic acid was studied from aqueous solutions. The structure of PDVB/PADETA IPNs was characterized by Fourier transform infrared spectroscopy, N_2 adsorption–desorption isotherms, weak basic exchange capacity, and swelling ratio, respectively. The results indicated that PDVB/PADETA IPNs possessed both hydrophobic and hydrophilic properties and they were much superior to the hydrophobic PDVB and the hydrophilic PADETA in adsorption of salicylic acid from aqueous solutions. The Freundlich model was more appropriate for fitting the equilibrium data than the Langmuir model and the isosteric enthalpy decreased with increment of the equilibrium uptakes. The breakthrough dynamic capacity of salicylic acid on PDVB/PADETA IPNs was 77.27 mg/mL wet resin at an initial concentration of 650.4 mg/L and a flow rate of 7.2 BV/h (bed volume, 1 BV = 10 mL) and the saturated dynamic capacity was calculated to be 93.28 mg/mL wet resin. One hundred and forty milliliter of 0.01 mol/L of sodium hydroxide (w/v) and 40% of ethanol (v/v) could regenerate the resin column completely. *AIChE J*, 60: 2636–2643, 2014
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Introduction

In 1970s, interpenetrating polymer networks (IPNs) were developed as a kind of novel polymeric materials and they were extensively applied in reinforced rubbers, toughened plastics, damping materials, coatings, and functional materials due to their unique forced compatibility.[1,2] Additionally, IPNs technology was proven an excellent polymer modification method for stable integration of two polymer networks with different properties or different functions by physical entanglements.[3–5] Due to the strong phase separation liability between the hydrophobic polymer networks and the hydrophilic polymer networks, the hydrophobicity or the hydrophilicity of the two polymer networks composed of the IPNs is similar at present, at least not opposite,[6–9] while few reports are presented for both hydrophobic and hydrophilic IPNs in the literature for the reason that the hydrophobic–hydrophilic IPNs cannot be directly synthesized by synchronous or sequential suspension polymerization.[10–12] We proposed that the phase separation liability will not be very serious as one of the hydrophobic polymer networks is transformed to the hydrophilic polymer networks by a chemical reaction after preparation of the hydrophobic–hydrophobic IPNs, and the hydrophobic–hydrophilic IPNs will be synthesized accordingly. In particular, this kind of hydrophobic–hydrophilic IPNs will be an efficient polymeric adsorbent for adsorption of the adsorbate with both hydrophobic portion and hydrophilic portion.

Salicylic acid can be easily produced from phenol and it is widely applied as the basic raw material for production of pharmaceutical intermediates such as aspirin (acetylsalicylic acid), 2-hydroxybenzamide, ethenzamide and so on. Additionally, salicylic acid is frequently used as a kind of

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cosmetic additive in the field of cosmetic industry as the added concentration of salicylic acid is very low (<1.5% in China) while it brings serious environmental problems at a high concentration. Salicylic acid can induce headache, nausea, and even affect the liver and kidney. Additionally, biological degradation of salicylic acid is not feasible from aqueous solutions due to the electron-withdrawing carboxyl group on the benzene ring.[13,14] Wastewater contaminated by salicylic acid and other volatile organic compounds (VOCs) is dark-colored and highly toxic. As a result, an efficient removal and recycling of salicylic acid from aqueous solutions has attracted many attentions in recent years.

In consideration of the molecular structure of salicylic acid, it has a hydrophobic benzene ring as well as a hydrophilic hydroxyl and carboxyl group. Moreover, the adjacent hydroxyl and carboxyl group can form intramolecular hydrogen bonding,[15] which makes salicylic acid a well-balanced molecule of hydrophobic portion and hydrophilic portion. The benzene ring of salicylic acid is highly hydrophobic, the same as the newly formed hexatomic ring between the carboxyl group and the phenolic hydroxyl group due to weakly intramolecular hydrogen bonding. However, the exocyclic the hydroxyl group of carboxyl group is hydrophilic.[15] As salicylic acid is diffused in the pores of a hydrophobic–hydrophilic polymeric adsorbent like hydrophobic–hydrophilic IPNs, the hydrophobic portion of salicylic acid will have a relatively strong affinity toward the hydrophobic polymer networks of hydrophobic–hydrophilic IPNs, whereas the hydrophilic portion of salicylic acid is more inclined to approach the hydrophobic–hydrophilic IPNs, and hence a much more enhanced adsorption of salicylic acid will be achieved on the hydrophobic–hydrophilic IPNs with respect to the single hydrophobic polymeric adsorbent like polydivinylbenzene (PDVB) or the single hydrophilic polymeric adsorbent like polyacrylamide.

As discussed above, in this study, we first synthesized a hydrophobic–hydrophobic PDVB/polymethylacrylate (PDVB/PMA) IPNs by a typical IPNs technology after preparation of the hydrophobic PDVB, the second hydrophobic PMA networks were then transformed to the hydrophilic polyacryldiethylenetriamine (PADETA) networks by an amidation reaction, and hence a hydrophobic–hydrophilic IPNs composed of PDVB/PADETA (PDVB/PADETA) were achieved. After characterization of PDVB/PADETA IPNs by Fourier transform infrared (FTIR) spectroscopy, N_2 adsorption–desorption isotherms, general chemical analysis and swelling ratio property, the adsorption performance of PDVB/PADETA IPNs toward salicylic acid were investigated in detail from aqueous solutions.

Experimental

Materials

Divinylbenzene (DVB) was purchased from Gray West Chengdu Chemical Technology (Sichuan Province, China) and its content was 80% (w/w), it was washed by 5% of sodium hydroxide aqueous solution (w/v) and deionized water, and then dried by anhydrous magnesium sulfate before use. Salicylic acid, phenol, and bisphenol A applied as the adsorbates in this study were analytical reagents and used without further purification. Industrial triallylisocyanurate (TAIC) was purchased from Liuyang Chemical (Hunan Province, China) and its content was 98% (w/w). Benzoperoxide and 2, 2-azobisisobutyronitrile (AIBN) were purified by recrystallization before use. Methylacrylate (MA), toluene, butyl acetate, diethylenetriamine (DETA), and *n*-heptane were also used in this study and they were all analytical reagents.

Synthesis of macroporous PDVB

Macroporous PDVB was prepared by a conventional suspension polymerization method described in Ref. 16. The organic phase solutions including DVB, the porogens (toluene and *n*-heptane, and they were 200% relative to DVB and the ratio was set to be 3:1, w/w) and the initiator (1% in relation to DVB, w/w) were added into a 0.5% of polyvinyl alcohol (PVA, w/w) aqueous phase solution with the temperature at 318 K. After adjusting an appropriate stirring speed, the temperature of the reaction mixture was maintained at 358 K for about 12 h. The gained PDVB polymeric beads were filtered from the reaction mixture, washed by hot deionized water for three times, and extracted by petroleum ether in Soxhlet apparatus for 24 h and then dried at 328 K for 8 h.

Preparation of PDVB/PMA IPNs

The macroporous PDVB polymeric beads were first swollen by a mixture of MA, TAIC, butyl acetate, *n*-heptane, and AIBN at room temperature for 24 h. Butyl acetate and *n*-heptane (250% relative to the monomers (MA and TAIC) and the ratio was 4:1, w/w) was used as the porogens, the ratio of MA to TAIC was defined to be 9:1 (w/w) and that of the monomers to PDVB was determined to be 1:1 (w/w). The swollen PDVB polymeric beads were then separated from the mixture solution and added into the 0.5% of PVA aqueous solution (w/w, 300 parts). At a moderate stirring speed, the temperature of the reaction mixture was resin to 358 K and the reaction mixture was kept at this temperature for 12 h. The resultant products PDVB/PMA IPNs were eluted by hot deionized water, extracted by petroleum ether for 24 h and dried at 328 K for 8 h.

Amidation of PDVB/PMA IPNs

Forty gram of dried PDVB/PMA IPNs was swollen by a superfluous DETA solution at room temperature for 18 h. After that, the temperature of the reaction mixture was risen to 403 K and the reaction mixture was retained at this temperature for 15 h. The polymeric beads were filtered from the reaction mixture and rinsed by 5% of sodium chloride aqueous solution (w/v) for three times and extracted by anhydrous ethanol for 8 h, and then dried at 328 K for about 8 h, and the PDVB/PADETA IPNs were obtained accordingly.

Preparation of macroporous PMA and PADETA

Macroporous PMA was prepared by a conventional suspension polymerization technique described in Ref. 16. MA is used as the monomer while TAIC was applied as the crosslinking reagent. Butyl acetate and *n*-heptane (the ratio was scaled to be 4:1, w/w) were applied as the porogens. The ratios of MA to TAIC and that of the porogens to the monomers were set to be 9:1 and 5:1 (w/w), respectively. The resultant PMA polymeric beads were amidated by DETA at 403 K for 15 h, and the macroporous PADETA was synthesized accordingly.

Characterization of the resins

The specific surface area, pore volume, and pore-diameter distribution of the resins were determined by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Tristar

3000 surface area and porosity analyzer. The total specific surface area and pore volume were calculated according to the Brunauer–Emmett–Teller (BET) model while the pore-diameter distribution was calculated by applying the Barrett–Joyner–Halenda (BJH) method to the N_2 desorption data. FTIR spectroscopy of the resins was recorded on a Nicolet 510P FTIR instrument in 600–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. The weak basic exchange capacity of the resins was measured according to the method in Ref. 16. The swelling ratio of the resins in different solvents was studied as follows. The resins were snapped after swelling in a solvent at room temperature for 24 h, the diameters of the resin in the dry state and in the swollen state were detected according to the snapped pictures, and the swelling ratio of the resins in different solvents was calculated by the following equation

$$R_v = (D_t/D_0)^3 \quad (1)$$

where R_v was the swelling ratio of the resins in different solvents, D_0 and D_t was the diameter of resin in the dry state and in the swollen state, respectively.

Equilibrium adsorption

Equilibrium adsorption of salicylic acid on the resins was performed at three different temperatures (293, 303, and 313 K, respectively) from aqueous solutions. About 0.1000 g of the resins was accurately weighed and mixed with 50 mL of salicylic acid solution at different initial concentrations. The initial concentrations of salicylic acid were preset to be 200.1, 400.2, 600.3, 800.4, and 1000.5 mg/L, respectively. The mixture solution was then continuously shaken at a desired temperature for 8 h so that the adsorption reached equilibrium. After that, the resins were filtered and the equilibrium concentration of salicylic acid, C_e (mg/L), was determined by UV absorption analysis performed on a UV-2450 spectrophotometer and the equilibrium capacity of the resins toward salicylic acid, q_e (mg/g), was calculated by conducting a mass balance of salicylic acid before and after the equilibrium adsorption experiment.

Dynamic adsorption and desorption

The resins were immerged in deionized water at room temperature for 24 h and then packed densely in a glass column (16-mm diameter) to assemble into a resin column. The volume of the wet resin column was 10 mL. The salicylic acid solution at an initial concentration of 650.4 mg/L was passed through the resin column at a flow rate of 7.2 BV/h and the residual concentration of salicylic acid from the effluent, C (mg/L), was dynamically recorded until it reached the initial concentration. After the dynamic adsorption, the resin column was roughly rinsed by 20 mL of deionized water and then a mixture solution composed of 0.01 mol/L of sodium hydroxide (w/v) and 40% of ethanol (v/v) was used as the desorption solvent for the dynamic desorption. Desorption solvent (200 mL) was passed through the resin column at a flow rate of 3.6 BV/h and the concentration of salicylic acid from the effluent was determined until it was about zero.

Results and Discussion

Characterizations of the polymeric adsorbents

Figure 1 displays the FTIR spectra of PDVB, PMA, PDVB/PMA IPNs, and PDVB/PADETA IPNs, respectively.

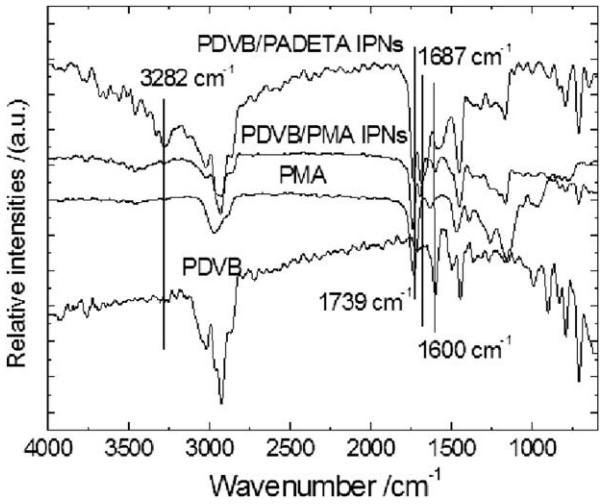

Figure 1. FTIR spectra of PDVB, PMA, PDVB/PMA IPNs, and PDVB/PADETA IPNs, respectively.

The FTIR spectrum of PDVB/PMA IPNs was completely superimposed by that of PDVB and PMA, the strong absorption bands of C=C stretching for the benzene ring of PDVB with frequencies at 1600, 1500, and 1450 cm^{-1} could be found in the FTIR spectrum of PDVB/PMA IPNs,[17,18] the very strong characteristic C=O stretching vibration for the ester carbonyl of PMA at 1739 cm^{-1} was also appeared for PDVB/PMA IPNs.[17] The FTIR spectrum of the obtained PDVB/PMA IPNs revealed that not any new chemical bonding was reformed between the PDVB networks and the PMA networks in addition to physical entanglements and the PDVB/PMA IPNs was real IPNs.

After amidation reaction of the PMA networks of PDVB/PMA IPNs with DETA, the vibration related to the C=O stretching for the ester carbonyl of PMA was sharply weakened, while a new strong band appeared at 1687 cm^{-1} in the FTIR spectrum of the obtained PDVB/PADETA IPNs and this vibration can be assigned to the C=O stretching of the amide carbonyl of PADETA.[17] In addition, another new band with frequency at 3283 cm^{-1} was also observed for PDVB/PADETA IPNs,[18,19] and which is concerned with the N—H stretching of the —NH— or —NH_2 groups. In particular, the general chemical analysis of the obtained PDVB/PADETA IPNs indicated that the weak basic exchange capacity of PDVB/PADETA IPNs was 1.808 mmol/g while that of the PDVB, PMA, and PDVB/PMA IPNs was determined to be zero. These results suggested the PMA networks of PDVB/PMA IPNs were transformed to the PADETA networks and PDVB/PADETA IPNs were synthesized successfully.

As shown in Figure 2, the N_2 adsorption capacities on PDVB, PDVB/PMA IPNs, and PDVB/PADETA IPNs were gradually decreased at the same relative pressure, which demonstrated that the BET surface area and the pore volume of PDVB were the highest while those of PDVB/PADETA IPNs were the lowest. In fact, the BET surface area of PDVB, PDVB/PMA IPNs, and PDVB/PADETA IPNs were measured to be 616.1, 325.3, and 239.9 m^2/g, and their pore volume were determined to be 1.205, 0.8244, and 0.5736 cm^3/g, respectively, These results implied that the IPNs technology makes the BET surface area and pore volume of the resins decreased and the amidation reaction induces a great decrease. The shape of the N_2 adsorption–desorption isotherm seems close to type-II classification, the N_2 adsorption

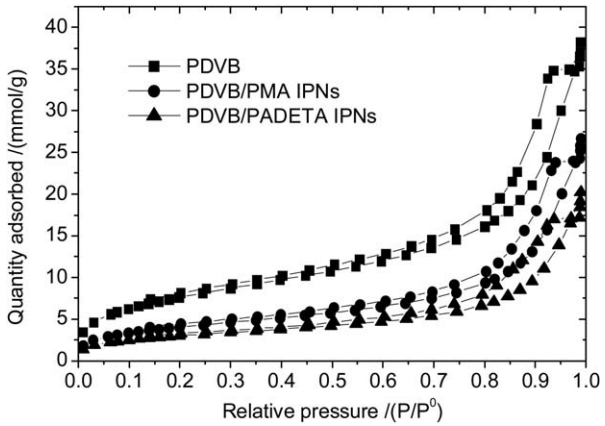

Figure 2. N_2 adsorption–desorption isotherms of PDVB, PMA, PDVB/PMA IPNs, and PDVB/PADETA IPNs, respectively.

capacity on the resins increased steadily with increment of the relative pressure at $P/P^0 < 0.05$, demonstrating that not any micropores are existent. A hysteretic loop between the adsorption and desorption curve at a medium relative pressure ($P/P^0 < 0.05$–0.95) suggests mesopores play a predominant role in the pore-diameter distribution of the resins. Moreover, a rapid increase of the N_2 uptakes at a relatively higher pressure ($P/P^0 > 0.95$) indicates that these resins have macropores. All of these analyses are accordant with the pore-diameter distribution of these resins in Figure 3.

Swelling properties of PDVB/PADETA IPNs in different solvents

The snapped pictures of PDVB/PADETA IPNs in the dry state, water, toluene, and benzyl alcohol were measured and the calculated swelling ratio of the resin in different solvents was summarized in Table 1. It is interesting to observe that PDVB/PADETA IPNs possess the different swelling ratio in different solvents. The swelling ratio of PDVB/PADETA IPNs in water was calculated to be 1.260 and which is very close to that in toluene (1.341), while the swelling ratio of PDVB/PADETA IPNs is surprisingly high in benzyl alcohol (2.391). As a matter of fact, water is a completely hydrophilic solvent, as PDVB/PADETA IPNs are immerged in water, the hydrophobic benzene ring of PDVB networks of

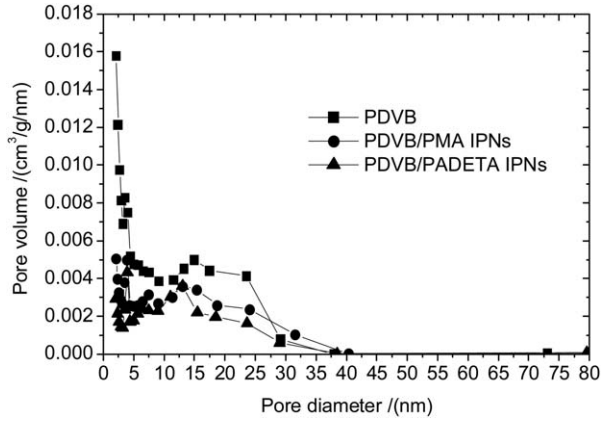

Figure 3. Pore-diameter distribution of PDVB, PMA, PDVB/PMA IPNs, and PDVB/PADETA IPNs, respectively.

Table 1. Swelling Ratio of PDVB/PADETA IPNs in Different Solvents

	Water	Toluene	Benzyl Alcohol
δ (SI)	47.3	18.2	23.8
Diameter of the resin	3.78	3.86	4.68
R_v	1.260	1.341	2.391

PDVB/PADETA will limit water molecules to enter the pores of PDVB/PADETA IPNs although the hydrophilic amide and amino groups of PADETA networks have a strong affinity toward water molecules, and hence a less swelling ratio of PDVB/PADETA IPNs will be achieved in water. Similarly, the hydrophilic amide and amino groups of PDVB/PADETA IPNs will prevent toluene molecules from swelling in the pores of the of PADETA networks despite the hydrophobic benzene ring of PDVB networks is more inclined to approach the toluene molecules as PDVB/PADETA IPNs is immersed in hydrophobic toluene, which also brings about a less swelling ratio of PDVB/PADETA IPNs in toluene.

Benzyl alcohol is both of hydrophobic and hydrophilic because benzyl alcohol has a hydrophobic benzyl group together with a hydrophilic alcoholic hydroxyl group. As far as the swelling of PDVB/PADETA IPNs in benzyl alcohol is concerned, a quite different phenomenon will be emerged accordingly. The hydrophobic benzyl group of benzyl alcohol will interact with the hydrophobic benzene ring of PDVB networks by hydrophobic interaction,[20,21] whereas the hydrophilic alcoholic hydroxyl group of benzyl alcohol tends to interact the hydrophilic amide and amino groups of PADETA networks by hydrogen bonding.[3,22,23] Moreover, π-π stacking resulted from the benzene ring of benzyl alcohol and the pendant benzene ring of PDVB networks will contribute to enhance the swelling of PDVB/PADETA IPNs in benzyl alcohol as well.[24,25] Therefore, the swelling ratio of PDVB/PADETA IPNs in benzyl alcohol is much higher than that in water and in toluene, which confirms that PDVB/PADETA IPNs has duple characters of hydrophobic and hydrophilic properties and it is a hydrophobic–hydrophilic IPNs.

Adsorption isotherms of different adsorbates on the resins

In this study, three adsorbates such as bisphenol A, phenol, and salicylic acid were selected for comparison of the adsorption on the resins from aqueous solutions. As observed from Figure 4 (a), the equilibrium capacities of bisphenol A on the resins decrease on a sequence of PDVB, PDVB/PMA IPNs, PMA, and PDVB/PADETA IPNs, and this sequence agrees with the BET surface area of the resins. The one $(CH_3)_2C$— group and two benzene rings are hydrophobic portion while the two phenolic hydroxyl groups are hydrophilic portion for bisphenol A, the hydrophobic portion should be in a dominant position than the hydrophilic portion and hydrophobic interaction may be the driven force for the adsorption of bisphenol A on the resins from aqueous solutions. Generally, an adsorbent with a higher BET surface area has a larger equilibrium capacity as the hydrophobic interaction is the main driven force,[16,26,27] and hence PDVB possesses the largest equilibrium capacity toward bisphenol A while PDVB/PADETA IPNs holds the lowest.

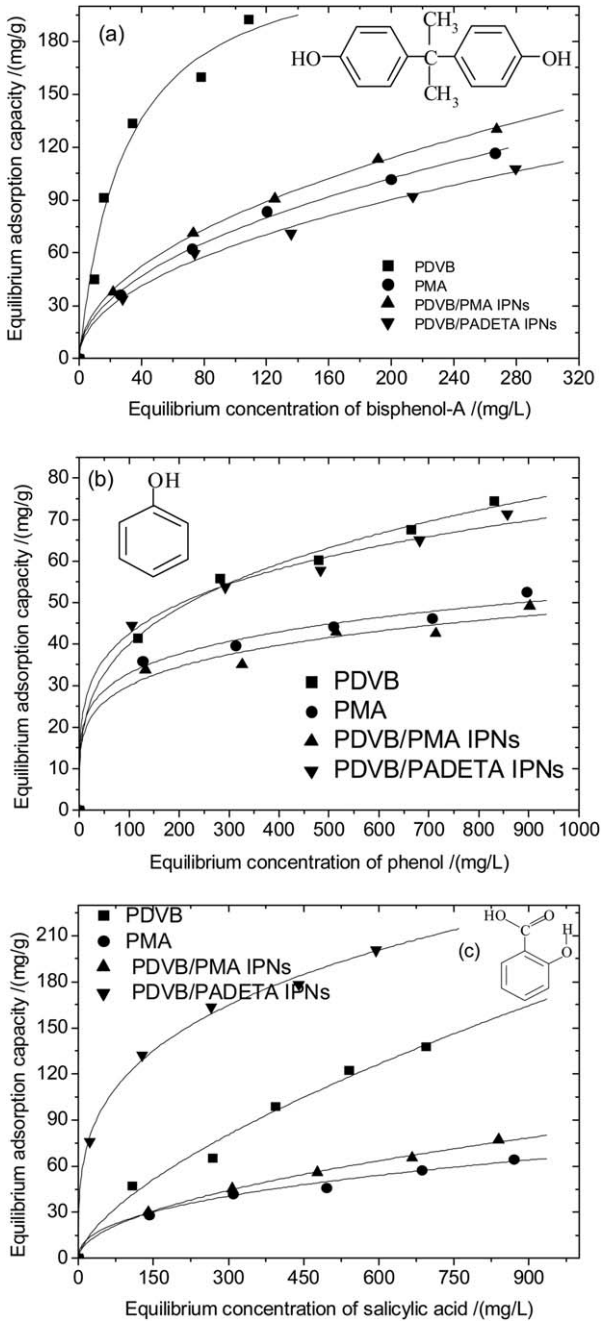

Figure 4. Equilibrium adsorption isotherms of (a) bisphenol A, (b) phenol, and (c) salicylic acid on PDVB, PMA, PDVB/PMA IPNs and PDVB/PADETA IPNs from aqueous solutions with the temperature at 293 K.

Figure 4b indicates a quite different phenomenon for the phenol adsorption on the resins from aqueous solutions. Although PDVB/PADETA IPNs has the lowest BET surface area among the four resins, the equilibrium capacity of phenol on PDVB/PADETA IPNs was quite larger than that on PMA, PDVB/PADETA IPNs and was almost identical to that on PDVB. In addition to the BET surface area, the polarity matching between the adsorbent and the adsorbate is also an important factor influencing the adsorption.[26,28] The benzene ring of phenol is the hydrophobic portion while the phenolic hydroxyl group is the hydrophilic portion, and hence phenol is a well-balanced molecule with hydrophobic portion and hydrophilic portion. PDVB/PADETA IPNs has both hydrophobic PDVB networks and hydrophilic PADETA networks; the hydrophobic benzene ring of phenol can be adsorbed on the PDVB networks of PDVB/PADETA IPNs by hydrophobic interaction and π-π stacking, while the hydroxyl group of phenol can interact with the amide and amino groups of the PADETA networks by hydrogen bonding, hence the polarity matching achieves an enhanced adsorption of phenol on PDVB/PADETA IPNs from aqueous solutions.

As consideration of the adsorption of salicylic acid on the resins from aqueous solutions (Figure 4c), the superiority of the hydrophobic–hydrophilic PDVB/PADETA IPNs toward the hydrophobic PDVB as well as the hydrophilic PADETA is perfectly presented. Salicylic acid should be a more well-balanced molecule with both hydrophobicity and hydrophilicity than phenol. As salicylic acid diffuses into the pores of PDVB/PADETA IPNs, the hydrophobic portion of salicylic acid will have a relatively strong affinity toward the hydrophobic PDVB networks, whereas the hydrophilic portion of salicylic acid is more inclined to approach the hydrophilic PADETA networks, and hence a much-enhanced adsorption of salicylic acid on PDVB/PADETA IPNs is achieved.

The equilibrium capacity of salicylic acid on PDVB/PADETA IPNs increases with increasing of the equilibrium concentration and it reaches 121.6 mg/g at an equilibrium concentration of 100 mg/L. As compared the equilibrium capacity of salicylic acid on PDVB/PADETA IPNs with the other adsorbents, it can be concluded that PDVB/PADETA IPNs is much superior to the macroporous polystyrene-type XAD-4 and X-5 resins,[19,29] macroporous polyacrylate-type XAD-7 and AB-8 resins[19] as well as the low-cost materials such as Bentonite and kaolin.[30,31] Moreover, in spite of the much lower BET surface area and the predominant meso/macropores rather than micro/mesopores, the equilibrium adsorption of salicylic acid on PDVB/PADETA IPNs is comparative to that on the reported hypercrosslinked resins such as HJ-L02 (a bisphenol A-modified resin),[32] HJ-G02 (a β-naphthol-modified resin),[33] HJ-D55 (a gallic acid modified resin),[34] and HJ-M01 (a diethylenetriamine-modified resins).[19] This encouraging result strongly suggests that the PDVB/PADETA IPNs being developed in this study is a promising replacement for many commercial adsorbents for adsorptive removal and recycling of salicylic acid and other VOCs from wastewater.

Adsorption isotherms of salicylic acid on PDVB/PADETA IPNs from aqueous solutions

As shown in Figure 5, all of the isotherms are type-I isotherms,[16] the temperature is favorable for the adsorption and a higher temperature results in a larger equilibrium capacity, implying an endothermic process.[16,35] Langmuir and Freundlich models are frequently adopted to describe the adsorption process.[36,37]

Langmuir model[36]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{2}$$

Freundlich model[37]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where q_m is the maximum capacity (mg/g), K_L is a Langmuir constant, K_F and n are the characteristic Freundlich constants.

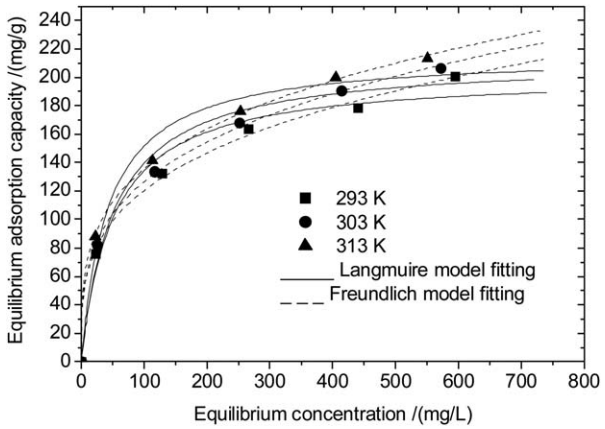

Figure 5. Equilibrium adsorption isotherms of salicylic acid on PDVB/PADETA IPNs from aqueous solutions with the temperature at 293, 303, and 313 K, respectively.

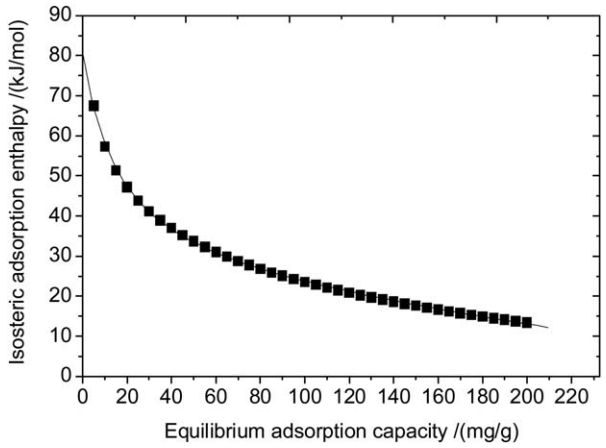

Figure 6. Plotting of the isosteric adsorption enthalpies vs. the equilibrium adsorption capacity for salicylic acid adsorption on PDVB/PADETA IPNs from aqueous solutions.

The isotherm data were fitted by the Langmuir and Freundlich models according to a linear fitting method, and the corresponding characteristic parameters K_L, K_F, n, and the correlation coefficients R^2 are summarized in Table 2. The experimental isotherm data are consistent with the fitting curves based on the Freundlich model because $R^2 > 0.99$, a higher temperature gives a greater K_F and n, implying the affinity between salicylic acid and the active sites of PDVB/PADETA IPNs is greater and the adsorption is more favorable at a higher temperature.

Following the Clapeyron–Clausius equation[27,38,39]

$$\ln C_e = \frac{\Delta H}{RT} + K\frac{1}{2} \tag{4}$$

here ΔH is the isosteric enthalpy (kJ/mol), T is the absolute temperature (K), R is the ideal gas constant, and K is a constant.

In this study, the three isotherms at 293, 303, and 313 K were used to make the ΔH plots. The isotherms were first converted to the isosteres, a plot of $\ln C_e$ vs. 1/T at a given equilibrium capacity and then the ΔH was calculated from the slopes of the isosteres according to Eq. 4. As exhibited in Figure 6, ΔH is positive, indicating an endothermic process.[16] The positive ΔH suggests that the adsorption of salicylic acid on PDVB/PADETA IPNs is probably not a physical process that may involve a weak chemical bond formation between the adsorabte and the adsorbent, which will be indirectly proven by the regeneration step performed in the subsequent section. It was impossible to regenerate the PDVB/PADETA IPNs resin column completely by deionized water or ethanol after the dynamic adsorption of salicylic acid. However, the resin column could be completely regenerated by purging with a mixture solvent composed of 0.01 mol/L of sodium hydroxide (w/v) and 40% of ethanol (v/v). Meanwhile, the ΔH decreases strongly with increasing of the equilibrium capacity, especially at a lower equilibrium capacity, indicating a high surface energetic heterogeneity,[39] and this surface energetic heterogeneity may be attributed to the strong polar interaction between the amide and amino groups of PDVB/PADETA IPNs and the hydroxyl and carboxyl groups of salicylic acid.

Dynamic adsorption and desorption process

Figure 7a is the adsorption breakthrough profiles for the dynamic adsorption of salicylic acid on PDVB/PADETA IPNs resin column. For the column operation, breakthrough dynamic capacity is more significant for judging whether the adsorbents can be applied in real field application or not than the saturated dynamic capacity. In this study, the breakthrough point was set to be $C/C_0 = 0.05$ and the breakthrough volume of salicylic acid on 10 mL wet PDVB/PADETA IPNs resin was 118.8 bed volumes and hence the breakthrough dynamic capacity was calculated to be 77.27 mg/mL wet resin.

After the dynamic adsorption, the PDVB/PADETA IPNs resin column was roughly rinsed by 20 mL of deionized water and then different solvents were used for the desorption process. The recovery efficiency of different solvents for desorption of salicylic acid from the resin column was displayed in Figure 8. It is evident that water can hardly desorb salicylic acid and only 14.4% of salicylic acid is desorbed from the resin column as water is applied as the desorption solvent. Ethanol can partly desorb salicylic acid from the resin column and a higher concentration of ethanol leads a higher recovery efficiency, and 45.8% of recovery efficiency is achieved as 75% of ethanol (v/v) is used for the desorption. Meanwhile, sodium hydroxide aqueous solution is very

Table 2. Isotherm Parameters for the Adsorption of Salicylic Acid on the PDVB/PADETA IPNs with the Temperature at 293, 303, and 313 K According to Langmuir and Freundlich Models

	Langmuir Model			Freundlich Model		
T (K)	q_m (mg/g)	K_L (L/g)	R^2	K_F ([(mg/g)(L/mg)$^{1/n}$])	n	R^2
293	215.0	14.76	0.9898	30.54	3.384	0.9944
303	224.7	14.97	0.9928	32.36	3.396	0.9980
313	230.4	17.03	0.9930	37.58	3.606	0.9990

effective for the desorption and 94.1% of salicylic acid can be recovered as 0.01 mol/L of sodium hydroxide (w/v) is utilized. In particular, a mixture solution composed of sodium hydroxide and ethanol can greatly improve the recovery efficiency and 99.3% of recovery efficiency of is achieved as a mixture solution of 0.01 mol/L of sodium hydroxide (w/v) and 40% of ethanol (v/v) is used as the desorption solvent and we used this mixture solution as the desorption solvent in the dynamic desorption. At a flow rate of 3.6 BV/h, only 14.0 BV of the desorption solvent is enough to regenerate the resin column completely and the dynamic desorption capacity can be determined to be 926.7 mg (Figure 7b), which is excellently coincident with the saturated dynamic capacity (932.8 mg) in the dynamic adsorption.

Conclusions

A novel PDVB/PADETA IPNs was prepared successfully and it possessed a duple character of hydrophobic and hydrophilic property. The adsorption of salicylic acid on PDVB/PADETA IPNs was much superior to the hydrophobic PDVB as well as the hydrophilic PADETA, and the adsorption of PDVB/PADETA IPNs was superior to much polymeric adsorbents and comparative to the hypercrosslinked resins. The Freundlich model is shown to be more suitable for fitting the equilibrium isotherm data than the Langmuir model and the isosteric enthalpy decreased with increasing of the equilibrium capacity. The breakthrough capacity of salicylic acid on PDVB/PADETA IPNs resin column was determined to be 77.27 mg/mL wet resin and saturated dynamic capacity was calculated to be 93.28 mg/mL wet resin, and 140 mL of 0.01 mol/L of sodium hydroxide (w/v) and 40% of ethanol (v/v) can desorb the resin column completely.

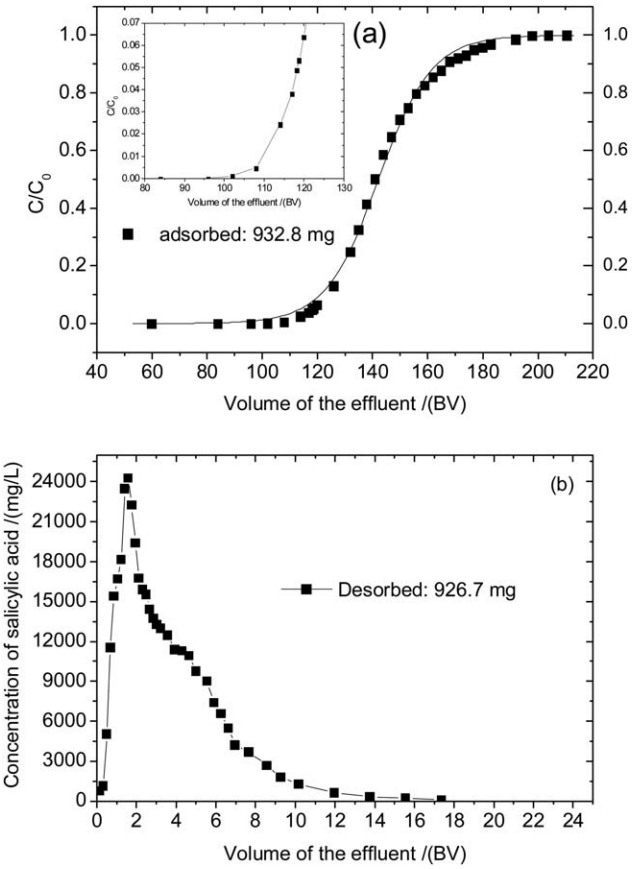

Figure 7. Dynamic (a) adsorption and (b) desorption curves of salicylic acid on PDVB/PADETA IPNs resin column from aqueous solutions.

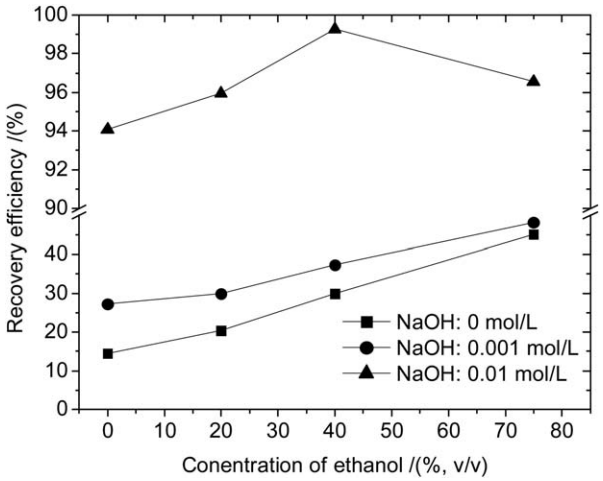

Figure 8. The recovery efficiency of different solvents for desorbing salicylic acid from the PDVB/PADETA IPNs resin column.

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